Chem Ed

EDITORIALLY SPEAKING

"Biophysical Science—A Study Program" is a book which should be brought to the attention of every undergraduate chemist. The nearly-600-page volume contains 61 papers which constituted the month-long Study Program conducted by the Biophysics and Biophysical Chemistry Section of the National Institute of Health at Boulder, Colorado, during the summer of 1959. John L. Oncley headed the editorial committee that prepared the present volume, published by John Wiley and Sons, Inc., in the fall of 1959. The papers first were published in two issues of *Reviews of Modern Physics*.

Publication of this volume should be a big step toward attaining the objective of the Study Program which was "to aid and encourage the further blending of concepts and methods of physical science with those of life science in the investigation of biological problems." More specifically it places under one cover lecture material which will "provide a timely research guide and a useful base on which to build new courses and seminars in biophysical science."

We see the serving of still another purpose in urging professors of undergraduate chemistry courses to examine this book and to make it available to their students. This is the ever-increasing importance of interdisciplinary training as the background for a scientific career. The essential theme illustrated by virtually every paper in this compilation is that expressed in the opening sentence of one contributor, "Biology is now in an exciting phase marked by the confluence of different disciplines of research in the attack on focal problems."

All who counsel undergraduates know how frequently they encounter the student who has made up his mind about his life work after having had a few credit hours in a subject. He then proceeds with fire in his eye to take all the offerings of that department to the complete exclusion of what he considers to be nonessential fringe activity in other fields. This kind of early enthusiasm for a specialty is educationally unfortunate for the individual, and the regrettable circumstance is that so many students feel that something is wrong if they do not have it. Lack of motivation may become a hindrance for a student if he is taking rigorous courses which appear to him to be far removed from the kind of problems he would like to attack for the rest of his life. He needs to be helped to see the relevance of training at a depth beyond superficiality in a variety of disciplines. This may be needed before he can even formulate the "focal problems."

After reading this book, no undergraduate majoring in biology will continue to think, as some do, that his career can be spent with microscope and microtome, using a little chemistry, only nodding to physics, and as a life devoid of the complications of mathematics. Also the eyes of many typical undergraduate majors in the physical sciences will be opened. Their disdain for the "frog-cutter-uppers" will evaporate when they realize the kind of attack now being made on the fundamental problems of bio-science: how does the living organism operate at the molecular or macromolecular level?

The picture drawn by the authors of these papers is one which should fascinate even the student with a beginner's grasp of organic and physical chemistry. The elucidation of structure by physical techniques that is starting to unravel the mysteries and uncover the consistencies in the properties of nature's macromolecules (the polypeptides, polysaccharides, and nucleic acid chains), promises exciting things in years to come. The emergence of understanding the correlation of structure and function in lamellar systems by applying the concepts useful in solid state physics is another demonstration of the fruitfulness of interdisciplinary approach. Another is the theoretical model built from thermodynamic and kinetic data to account for reciprocity between the contraction of muscle and its catalyzing the hydrolysis of energy-rich ATP.

Seldom has the growing edge of knowledge in a broad field been so well described as in this book. The excellent format, profusion of well-chosen figures and photographs, abundant references, and selected bibliographies all complement the lucidity of the presentation. It deserves a conspicuous spot in any library frequented by science students.

H. A. Wilhelm
Ames Laboratory of the U.S.A.E.C.
and the Institute for Atomic Research
Iowa State University, Ames

Development of Uranium Metal Production in America

Mineralogists in the early years of the eighteenth century were puzzled in the classification of a black dense mineral from Joachimsthal in Bohemia and from Johanngeorgenstadt in the Erzgebirge of Saxony (*1*, *2*). The mineral was referred to as "Schwarz Beck-Erz" by F. E. Brückmann in 1727. J. G. Wallerius in 1747 used the name "Beckblende" in his classification of the mineral among the zinc ores, and he described it as a pitchlike zinc-blende. In 1758 the Swedish mineralogist A. F. Cronstedt, who is considered as the founder of the chemical system of mineralogy, listed the mineral under the name of "Swart Blende," and recognized that in Germany at that time it was also known as "Pechblende." The classification of this mineral among the zinc ores was retained by I. Eques von Born in 1772 and by M. T. Brünnich in 1777. A. G. Werner after examining pechblende for fracture characteristics, hardness, and density classified it as an iron mineral. As late as 1789 he preferred to name the mineral "Eisenpecherz" although he suggested that the iron might be present as a tungstate.

In 1759 the sixteen-year-old Martin Heinrich Klaproth, who later discovered uranium, began a five-year apprenticeship in an apothecary shop (*3*). Later he worked in the laboratory of Wendland's Pharmacy and in The Rose Pharmacy, both in Berlin. After he purchased a laboratory in Berlin, he made many contributions to analytical and mineralogical chemistry. He was considered by some to be the greatest analytical chemist of his time.

Klaproth's investigations of minerals included samples of pechblende (pitchblende) from a mine in the Erzgebirge of Saxony. When samples of pitchblende were treated with nitric acid, he obtained solutions that gave yellowish precipitates on neutralization with potash. This precipitate was soluble on addition of excess potash. The color of the first precipitate varied somewhat, depending on the particular sample of pitchblende he employed. By further work he obtained the yellow precipitate in fair purity and demonstrated that pitchblende contained a substance that was not related to zinc, iron, or tungsten. He also showed that this mineral contained an element that was not like any of the recognized elementary substances of that time. In view of this discovery, Klaproth considered that the names Pechblende, Eisenpecherz, and others then in use were not applicable to this mineral and suggested that it be named "uranit" as a sort of memorial to the discovery of the planet Uranus by Herschel a few years earlier (1781).

First Preparation of Uranium Metal

Having isolated the yellow oxide of this new element, Klaproth set up experiments with the object of preparing the free element. This oxide was mixed with linseed oil to give a pasty mass. The oil was then burned gently and a black heavy powder remained. This powder was then placed in a crucible lined with charcoal dust. The remaining space in the crucible above the charge was filled with more of the charcoal dust. The crucible was then covered with a lid and placed in a moderately heated oven. After removing the crucible from the oven, the substance, in the form of a heavy mass of loose consistency, was recovered from the charcoal dust. Klaproth believed this to be the metal and described the particles as black dust with a slight luster. In a similar test in which calcined borax was also added in making up the charge, the oven was heated to its highest temperature. Klaproth considered that the agglomerated product from this treatment consisted of small porous grains of metal. The porous mass, which had a bulk specific gravity of 6.44, was easily broken down to a powder by filing. From the properties observed, he considered the element to be somewhat of a half-metal.

The results of Klaproth's early experiments on pitchblende and uranium were presented before the Berlin Academy of Sciences (*4*). Although it was shown later that Klaproth did not actually prepare the free metal, he is credited with the discovery in 1789 of the element uranium. Uranium was the twenty-fourth element to be discovered.

During the half century following Klaproth's announcement of his discovery of uranium, others repeated the process he employed in preparing what he believed to be elementary uranium metal. The process was accepted somewhat as standard, and little else was done toward preparing uranium in elementary form during this period. J. A. Arfwedson made hydrogen reductions of the green oxide and of a double potassium-uranium chloride, and the products were interpreted as containing metallic uranium. It was considered that this new element presented not the slightest difficulty of production in the metallic state. J. J. Berzelius obtained the same material by heating the oxalate in a closed container.

However, Berzelius, from certain anomalous data on this new element, held some reservations with regard to the elementary nature of the material considered as the metal. Consequently, he treated the assumed metal with distilled potassium but obtained no further reduction.

It remained for the French chemist Eugene Peligot in the early part of the next half century to unravel methodically much of the chemistry of uranium and for the first time to prepare the element in its true

metallic form (*5*). In 1841 Peligot reported the results of some careful studies on uranium. He had concluded that the material considered to be uranium metal by earlier workers was not a simple body and that it contained oxygen. Also he made the assumption that uranium occurs in some compounds as a part of a radical and in others as a simple element like many other metals.

In the course of his experimental work, Peligot passed chlorine over a heated mixture of carbon and uranium oxide. Instead of obtaining the familiar yellow chloride of uranium, he obtained a uranium chloride that sublimed and crystallized into beautiful dark green, regular octahedra. Experimental work with this crystalline material revealed that the behavior of the uranium part of this compound differed from that in the chlorides in earlier work. Analytical results showed that 100 parts of this compound contained 110 parts of the two elements chlorine and uranium, in accordance with the accepted analytical procedures. Peligot demonstrated that this anomaly was due to the erroneous conclusions of Klaproth and others that they had obtained the free element.

Peligot passed chlorine over a heated mixture of carbon and of "uranium" as prepared by the earlier techniques and obtained carbon dioxide and carbon monoxide, as well as the green sublimate of uranium chloride. The presence of oxygen in the products proved that the metal by earlier methods was merely a lower oxide of uranium and not elementary uranium. He then began work on the isolation of metallic uranium.

The green crystals of uranium chloride were employed in a reduction with potassium metal. The chloride is quite hygroscopic and the potassium reacts with air, so the preparation of the charge has to be made rapidly. Two parts of the chloride and one part of potassium were placed in a platinum crucible. The lid of the crucible was wired on and, for safety, this assembly was placed inside a larger crucible. Gentle heating of the crucible and its contents was sufficient to ignite the charge, causing a reaction which took place with the release of such energy that the entire crucible became incandescent. After cooling, the products of the reaction were treated with water to dissolve the KCl and give a residue of uranium metal which was partly in the form of black powder with some agglomeration. This product was decidedly metallic and differed considerably in chemical and physical properties from the "uranium" prepared by the earlier workers. It was then, in 1841, that Peligot prepared uranium metal for the first time.

Peligot then turned his attention to the determination of the atomic weight of uranium and arrived at a value of about 120. Experiments of others at the time supported Peligot's value. However, in 1869 the Russian scientist Dmitri Mendeleev arranged all known elements in a table according to the properties of the elements. He found that uranium as atomic weight 120 did not fit into his arrangement, but if he assumed an atomic weight of 240, the element fit nicely into a subgroup with chromium, molybdenum, and tungsten. Mendeleev assumed that the accepted atomic weight of uranium at that time was only half of the true value (see Zimmermann (*6*)). Subsequent work confirmed his assumption, and the placing of uranium in the family with tungsten and molybdenum, where it remained for many years, gave a basis for certain investigation of uranium metallurgy in the early part of the twentieth century.

Uranium Production Prior to the Atomic Age

During the half century following Peligot's first preparation of uranium metal very little was done toward developing new methods. Peligot in 1856 substituted sodium as the reductant of uranium chloride in place of potassium and added potassium chloride to the charge. He also heated the products to a sufficiently high temperature to obtain small globules of metallic uranium. In 1883 Zimmermann (*7*) employed a very similar process in preparing uranium metal for a study of its properties. He placed a layer of sodium chloride on the bottom of a cylindrical iron vessel 14 cm in height and 9 cm in outside diameter. On this layer he placed pieces of sodium metal and covered the sodium with more sodium chloride. He quickly added the uranous chloride, which is very hygroscopic, and covered the charge with more sodium chloride. The lid to the iron vessel was screwed on and the vessel placed in a charcoal fire. He found that heating the vessel to a dark red heat gave powdered uranium, but if he increased the temperature to a white heat the uranium fused into larger particles.

More than a century after Klaproth first tried to prepare uranium metal by the reduction of the oxide with carbon, the French chemist Henri Moissan showed that the metal could be obtained by this reaction at higher temperatures than those employed by Klaproth. In 1893 Moissan (see Mellor (*2*)) reported experiments in which he obtained a metallic ingot by heating the charge in a carbon crucible in the electric carbon tube furnace. In one of his experiments, a charge of 40 g of sugar charcoal mixed with 500 g of U_3O_8, when so heated, yielded an ingot weighing 350 g. However, the metal formed by this process always contained sufficient carbon to cause it to be brittle.

In 1896 Moissan obtained powdered metal by reacting sodium with a double chloride of sodium and uranium, employing the bomb technique of Zimmermann. Moissan also obtained uranium metal powder by the electrolysis of fused sodium uranium hexachloride.

In the closing years of the nineteenth century and first two decades of the twentieth century an increasing number of investigators (see Mellor (*2*) and Hampel (*8*)) worked on methods for preparing uranium metal without making any marked improvement over earlier work. Much of the work was on previously reported methods; however, a number of studies were made on the reduction of uranium oxide by calcium vapors and by aluminum, but they did not result in a satisfactory process for preparing good metal. All of the work that has been found reported in the literature on the preparation of uranium metal up to the year 1920 was that of European investigators.

A number of developments in science during the closing years of the nineteenth century and the early years of the twentieth century indirectly contributed very much to the early success of the uranium metal phase

of the atomic energy program, which was yet to come.

In 1896 the French physicist Henri Becquerel discovered radioactivity, which led directly to the discovery by Pierre and Marie Curie in 1898 of radium in uranium ores. The demand for radium that developed in subsequent years resulted in the locating of uranium ore bodies, the developing of mining operations, and the stock-piling of tons of crude uranium oxide. Also in this period, metallurgists were awakening to the possibilities of alloy additions to steel. The use of vanadium in steels brought about the stock-piling of more uranium oxide as a by-product of the treatment of some vanadium ores.

Much of the work involving uranium metal, following the developments in the years at the turn of the century, was based on the assumed relationship of the properties of uranium to those of molybdenum and tungsten, as suggested by the relative positions of these elements in the periodic table of Mendeleev. The special properties of the high-speed tool steel developed in 1898 by Taylor and White depended on the presence of several per cent of tungsten. Incandescent filaments of electric lights were made of tungsten. X-ray tubes employed tungsten targets. The carbide dies and cutting tools that were developed in Germany and that gave some factories of that nation increased production during World War I contained a high percentage of tungsten carbide. In all of these and in some other applications, tungsten (which is below molybdenum in the table) was superior to molybdenum; therefore, it was assumed by periodic table relationships that uranium, being below tungsten in the family, had a fair chance of being even superior to tungsten for such applications.

American Production

It was not until after two decades of the 20th century had passed that interest in possible uses of uranium metal began to get the attention of a few scientists in America. Then, within the period of a few years, most of the methods for preparing uranium metal that had been reported in the earlier literature were reinvestigated in America (see Hampel (*8*)), especially in the research laboratory of the Lamp Division of Westinghouse Electric Corporation where some new and improved techniques were developed. In 1922 J. W. Marden of Westinghouse obtained a patent on a process for reducing uranous halides with aluminum. This was the first published evidence of research on uranium metal preparation in this nation. In the ten-year period following this, the activities on uranium metal preparation in America far exceeded those reported in the rest of the world.

R. W. Moore of the General Electric Company reported in 1923 some results of his work on uranium metal preparation. He employed the sodium reduction of UCl_4 to obtain metal powder which he then pressed into pellets. These were heated by an arc to give some massive pieces of uranium that could be cold rolled into sheets.

Marden in 1926 reduced uranium oxide with magnesium under pressure at an elevated temperature. He studied the reactions between uranous chloride and sodium in the presence of a flux such as $CaCl_2$ between uranium oxide and aluminum. Patents were granted to Marden in 1927 on processes based on these studies. The next year he obtained a patent on the use of halide fluxing agents in the reduction of U_3O_8 with calcium metal. M. N. Rich, also of Westinghouse, was granted a patent in 1927 for a similar process in which a calcium-magnesium alloy was used as the reductant.

In the meantime a process for producing massive uranium metal was developed at the University of New Hampshire. J. C. Goggins, *et al.* (*9*) in 1926 published the results of research work on calcium reductions of uranium oxide and of uranium tetrachloride. In part of this research they employed a bomb process in which an alundum crucible within a steel bomb was charged with a mixture of uranium tetrachloride and calcium metal. The bomb was evacuated and then heated by electrical resistance heaters to the ignition temperature of the charge. The reaction was sufficiently exothermic to fuse the products, uranium metal and calcium chloride. After cooling the bomb to room temperature, a massive lump of uranium weighing about three pounds was recovered. Very little was reported on the properties of this metal, but from the limited analytical data included in the report, it appears that the metal was of good quality. This process for uranium metal, referred to later as the "James Process," was the first ever developed that was capable of producing massive uranium metal of possibly good quality by merely preheating the charge. This process developed at the University of New Hampshire had larger scale potentialities; however, the difficulties in the preparation of and the hygroscopic nature of anhydrous uranium tetrachloride were factors that posed as major disadvantages.

F. H. Driggs and W. C. Lilliendahl (*10*), also of Westinghouse, did work on the electrolysis of uranium metal from fused salt baths. Their process, which was described by patents issued in 1928 and by journal articles in 1930, was the electrolysis of KUF_5 in a $CaCl_2$-NaCl fused salt bath. The uranium was deposited as a granular mass on a metal cathode. The granular uranium was chipped from the electrode and recovered by leaching and washing to remove the occluded salt. Careful drying yielded the product as loose metal granules. Subsequent operations employing some powder metallurgy techniques, followed by vacuum induction melting, gave good quality uranium metal that could be fabricated into wire and sheet.

In 1931 Marden was issued a patent on a process in which the KUF_5 or other uranium halide was reduced with calcium metal in the presence of $CaCl_2$. This process was designed to give metal powder, with the purpose of the $CaCl_2$ being to assist in the control of metal particle size. By powder metallurgy techniques, ductile massive metal was prepared from these particles.

In the early uranium metal program at Westinghouse, the process based on the calcium reduction of uranium oxide in the presence of $CaCl_2$ was developed adequately to give workable solid uranium metal. However, interests of the workers at Westinghouse by 1931 were centered essentially on the fused salt electrolysis of KUF_5. Improvements were made in this latter process for uranium in the years that followed, but by the

end of the 1930's their uranium metal preparation was still operating on a laboratory bench scale.

P. P. Alexander (*11*) reported in 1938 the development of a uranium metal process which had been put into operation on a small scale at Metal Hydrides, Inc. The process was designed to be readily expandable to somewhat larger scale operations should the demands for a commercial grade of uranium metal develop sufficiently. The work on the development of uranium was actually started by Alexander in connection with a thesis at MIT in 1932. The process, which evolved from this thesis and further work in the years following, depended on the reduction of uranium oxide with calcium hydride.

In this process, a mixture of finely divided calcium hydride and calcined uranium oxide is charged into a steel or other metal container and heated to about 970°C. At this temperature the calcium hydride dissociates and the active calcium reduces the uranium oxide to give small particles of uranium metal. After completion of the reaction, the contents of the reactor are cooled under vacuum conditions. The finely divided uranium metal is recovered by leaching out the calcium oxide and collecting the wet powder on a filter. The powder is then dried in a vacuum and subsequently pressed into shape and sintered to give metal with fair density.

The metal prepared by Metal Hydrides in 1938 generally contained 98% by weight uranium, and it had been observed to fuse in a vacuum in the temperature range of 1250–1350°C. On the basis of this observation Alexander (*11*) believed that the melting point of pure uranium metal was possibly not higher than 1200°C.

Uranium metal was intermittently produced in America in 1939, on essentially laboratory scales, at both Westinghouse Electric Corp., Bloomfield, New Jersey, and at Metal Hydrides, Inc., Beverly, Massachusetts. Westinghouse was then employing the electrolytic process of Driggs and Liliendahl and had been supplying small amounts (essentially gram quantities) of metal in the form of wire and sheet to scientists for miscellaneous experiments for a number of years. Metal Hydrides had been supplying equally small quantities by P. P. Alexander's process for the same purposes but in the form of sintered metal compacts. In all, the total production of uranium metal to 1939 by both of these companies had amounted to perhaps not more than 10 pounds.

Atomic Energy on the Horizon

The year 1939 was just 150 years after the discovery of the element uranium by Klaproth in 1789. It was also the year in which Otto Hahn and F. Strassman, who were experimenting with neutron bombardment of uranium, reported results that were explainable by a fission process. As word spread concerning these experiments, they were quickly checked in other laboratories in Europe and America. Nuclear fission was confirmed, and some scientists began to visualize the possible realization of atomic energy through a self-sustaining fission chain reaction. As more experiments were hurriedly made the possibility of such a chain reaction appeared brighter (*12, 13*).

A number of scientists in America urged that the research on nuclear energy then being carried on in this nation by only a few universities be strongly supported by the Federal Government. Scientists, especially Leo Szilard, Enrico Fermi, and Eugene Wigner, believed that enormous energy tied up in the atom could be released and become a major factor in our national security. Through most of 1939, all of 1940 and most of 1941, many scientists (including Szilard, Fermi, Wigner, E. O. Lawrence, G. T. Seaborg, A. H. Compton, Vannevar Bush, and others) were active in supplying and interpreting data and in pressing for greater federal support.

Early attempts by G. B. Pegram and Fermi to interest the Navy Department in a nuclear energy program were not very encouraging. Szilard and Wigner stimulated a series of moves that eventually led to government support by first calling on Einstein to help their cause. In the summer of 1939 these three outstanding scientists discussed the matter with Alexander Sachs, an economist and personal friend of President Roosevelt. In the fall of 1939 Sachs, supported by a letter signed by Einstein, pointed out to the President some of the considerations of atomic energy relevant to national security. Late in 1939, the President, having thus been briefed on the possible significance of atomic experiments and of the deep concern of outstanding scientists in the field, appointed an Advisory Committee on Uranium with L. J. Briggs of the National Bureau of Standards as Chairman. This committee, known as the Uranium Committee, was organized to look into developments in the atomic energy field as regards national security. Financial support by government agencies for the needed investigations was meager, however, through mid-1940.

In June of that year, the National Defense Research Committee, with Vannevar Bush as Chairman, was set up by the President to promote work on various potential applications of science to national security, and the Uranium Committee was then reconstituted as one of the subcommittees of the NDRC. Near the end of 1940 the first sizeable contract for government support of research pertinent to an atomic program was approved by NDRC. As more scientific data were obtained and the trail got hotter, more and bigger government contracts were granted for research on phases of atomic energy.

As developments came, responsibilities increased sufficiently to make it advisable by the summer of 1941 to increase the membership of the Uranium Committee and form subcommittees on various aspects of the atomic program. Thereafter this committee became the Uranium Section or S-1 Section of NDRC. Scientific evidence indicating the potentialities of the atom continued to mount. Earlier the atom had been considered essentially as a source of power, but by December, 1941, the evidence strongly supported its use as a direct weapon of immense magnitude.

Plans were then proposed for the reorganization and further expansion of operations which brought the setting up of a Planning Board and the transfer of the Uranium Section from the NDRC to the Office of Scientific Research and Development as the S-1 Section of OSRD. With reorganization in the administration of the program still in progress, it was concluded

on December 6, 1941, that the U. S. Government should be requested to support an all-out effort on an atomic energy program.

Only near the end of this short preliminary period of intense scientific research and conference activity concerning uranium was there more than a somewhat casual increase in attention given to uranium metal procurement. A few scientists connected directly with the field of nuclear research had, in 1941, shown some concern about the uranium metal situation. The Bureau of Standards, at the request of Briggs (Chairman of the Uranium Committee), had been investigating the preparation of uranium metal. Massive metal had already been prepared in this effort by C. J. Rodden (*14*) in a study of the "James Process" (*9*). Rodden had found that the melting point of uranium, which was generally believed to be around 1850°C, was actually at a much lower temperature and in the range indicated earlier by Alexander (*11*). During 1941 a number of scientists including Fermi, Szilard, and Pegram of Columbia University had made exploratory contacts with the potential producers regarding uranium metal preparation and quality.

Because of purity problems, especially boron content of the metal, and uncertainty at the time regarding the amount of effort to be placed on the program, essentially no expansion of operations had yet gotten under way. So when the momentous December 6, 1941, came along, uranium metal production in America was still measured in gram or ounce quantities.

At this point, just 100 years after Peligot first prepared metallic uranium, the demand for that metal skyrocketed to pound quantities, with earliest possible deliveries. Production could not, however, be immediately expanded to fulfill all requests by the scientists for metal. Nevertheless, Westinghouse and Metal Hydrides had developed considerable "know how" with their processes and, consequently, through concentrated effort were able, at relatively early dates, to supply metal urgently needed for experiments so important to charting the future course of the atomic energy program in America.

It is interesting to note here that one of the many consequences of the atomic energy program was the demonstration that uranium does not even belong with the family of chromium, molybdenum, and tungsten in the periodic table. Experiments with uranium metal and some of its alloys had already shown, however, that uranium did not appear to have a close metallurgical relationship with these metals. Much of the incentive to the metallurgists for the earlier developments in uranium metal processes in America had been based on the assumption that uranium was a member of this family. Consequently, through the limited knowledge of earlier scientists, the atomic energy program in America was aided materially by the resulting early availability of experimental quantities of uranium metal.

Expansion of Uranium Metal Operations, Early 1942

As a result of the over-all reorganization of the administration for the atomic energy program of the nation late in 1941, a number of special projects were set up to develop methods for the production of concentrated fissionable material in quantity. One of these projects, the Plutonium Project, was organized and directed by Arthur H. Compton with assistance of Richard L. Doan and Norman Hillberry. The central headquarters office and laboratories were established in February of 1942 on the campus of the University of Chicago. This plutonium enterprise was then given the code name "Metallurgical Project" as sort of a wartime disguise for the nuclear development studies that were in the plans. The laboratory at Chicago was then named the "Metallurgical Laboratory," and Doan was appointed as its director.

On the basis of a few experiments, scientists were proposing nuclear reactors in which they envisaged self-sustaining fission chain reactions of uranium-235 atoms that would supply extra neutrons for converting uranium-238 atoms to plutonium-239. This plutonium, which no one had ever seen and only a very limited number of scientists had heard of, was to be generated in quantities sufficient to serve in a seemingly visionary atomic bomb, a bomb that would be a million times more powerful than conventional explosives.

It was this phase of the atomic program for which tons of normal uranium metal would be needed. The Metallurgical Project, however, in the over-all national organization did not officially have the responsibility of uranium metal procurement. The scientists close to this project in its early stages fully appreciated the importance of metal availability and were compelled by their convictions to investigate and expedite the metal production program.

The Plutonium Project scientists' early concern regarding the uranium metal situation can be exemplified by noting that, with the many pressing matters of the time, two Nobel Prize physicists, E. O. Lawrence of the University of California and A. H. Compton of the University of Chicago, with L. J. Briggs of the National Bureau of Standards, visited the Laboratory at Metal Hydrides on January 14, 1942, to discuss with P. P. Alexander (*15*) some means for obtaining pure uranium metal in quantity at an early date. Alexander began an expansion of uranium production facilities soon afterwards. Also in January, 1942, J. W. Marden at Westinghouse was approached by scientists regarding production of uranium metal of sufficient purity and in sufficient quantities to be of interest for proposed chain reaction experiments at Princeton University. By February 17, 1942, Westinghouse had supplied H. D. Smythe, E. Wigner, E. C. Creutz, and their associates at Princeton with a total of 307.5 g of high purity dense uranium metal.

The early orders for uranium metal pressed the laboratory scale operations to their limits at both Westinghouse and Metal Hydrides. Filling an order for 10 kilograms of ingot metal at Westinghouse was a major operation in the spring of 1942. Furthermore, these companies were approached in early 1942 to consider expanding their production to almost astronomical proportions involving tons of metal. In addition to the normal problems of expanding from bench operations to plant scales, the problem of certain trace impurities that affected markedly the nuclear properties of the metal was of great concern. In normal commercial production, trace impurities are

generally considered to have negligible effects on the ordinary physical properties of metals, but for neutron economy some impurities were to be present in not more than fractional parts per million in the uranium metal. Specifications on some of the impurities were even set at values that were below the range of analytical techniques at the time.

Boron was an impurity that plagued the producers in the early work for the atomic program. Westinghouse was able to reduce the boron content of the final metal adequately by employing low boron materials in the electrolytic bath and allowing the electrolyte to stand in the fused condition prior to starting the electrolysis. A "dummy" electrolysis prior to the main run was also effective in reducing the boron.

Alexander of Metal Hydrides, Inc., through exchanges of ideas with Szilard and others, had given some consideration in 1941 to expanding his uranium operations, but Rodden of the Bureau of Standards then found this metal to contain boron in amounts that made it useless for reactor purposes. The major source of this boron, Rodden found, was the calcium metal used in preparing the calcium hydride employed in the reduction. Rodden had earlier, in connection with his work on the "James Process," purified calcium by vacuum distillation. To help solve the impurity problem at Metal Hydrides, the Bureau of Standards by early 1942 had equipment set up at the Beverly plant to distill the calcium. The boron problem was then greatly reduced although not completely eliminated at Metal Hydrides.

The metal production project at Westinghouse was directed by J. W. Marden who was assisted by W. C. Lilliendahl (co-inventor of the Westinghouse electrolytic process), G. Meister, R. Nagg, D. M. Wroughton, and N. C. Beese. The process (*8*) used in early 1942, as shown schematically in Figure 1, started with uranyl nitrate solution. The uranium was reduced by an organic compound with aid of the actinic rays of the sun to give uranous ions. Potassium and fluoride ions were also present in the solution, and a green salt, KUF_5 was precipitated. The green salt was recovered and added to a fused salt bath of $CaCl_2$ and NaCl contained in a graphite crucible which served as the anode. A molybdenum bar cathode in the electrolytic bath collected the metal as a granular deposit. The molybdenum bar with the clinging deposit of uranium, wet with fused salt, was withdrawn from the bath and allowed to cool. The deposit was then removed from the electrode, broken up, washed, dried, and the metal powder pressed into briquettes that were subsequently vacuum-induction melted and cast in thorium oxide crucibles.

At the suggestion of the Princeton group, beryllium oxide crucibles for the melting and casting of uranium metal were tested by Marden in March, 1942, and subsequent operations employed beryllia instead of thoria crucibles in uranium melting at Westinghouse.

The quality of the Westinghouse metal was generally very good since careful control of the quality of the materials going into the operation was well organized early in their metal expansion program. Quantity production was the main problem and although ultraviolet lamps were put into operation by the Westinghouse people to supplement natural sunlight in the production of KUF_5, the dependence of the major part of this production on sunlight was a definite bottle-

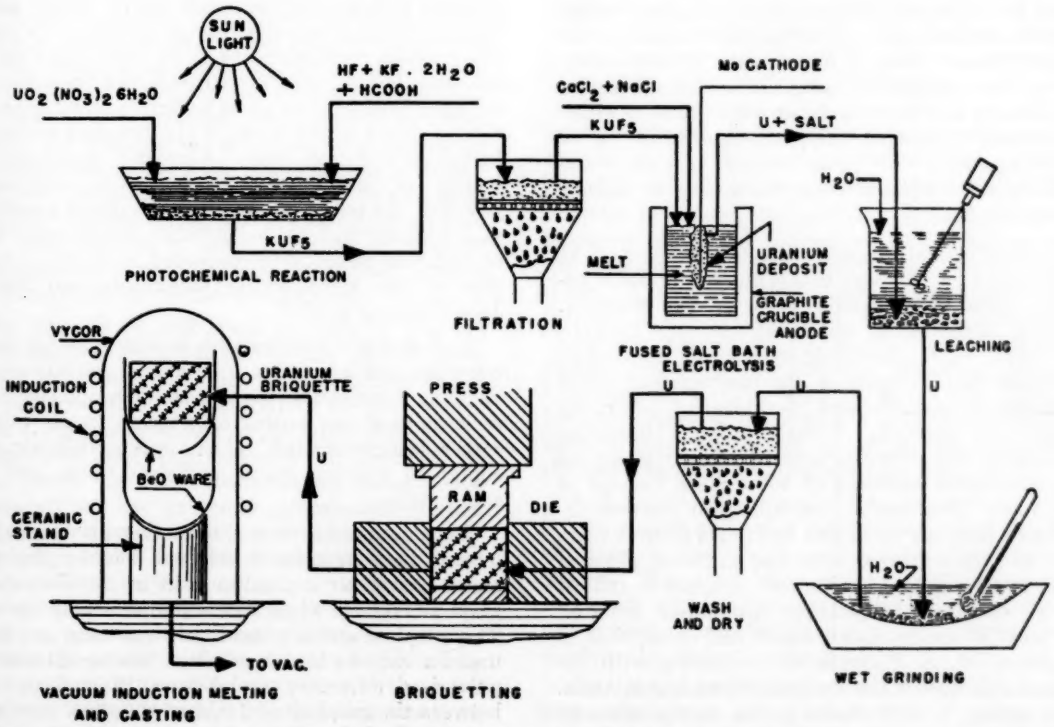

Figure 1. Schematic flow diagram of Westinghouse electrolytic process for uranium metal.

neck in the process. This sunlight operation was carried out on the roof of one of their buildings at the Bloomfield, New Jersey, plant. After expanding this operation in the spring of 1942 to make more green salt, the sun failed to shine on the roof for a number of days in succession. The uncertainty of sunlight for production at this plant brought about serious consideration for the construction of additional KUF_5 production facilities in Arizona. However, by late summer of 1942 production of UF_4, which it was found could replace KUF_5 in the Westinghouse electrolytic process, began to increase rapidly at other installations and the Arizona sunlight project was dropped.

Metal Hydrides' uranium production was under the direction of P. P. Alexander, assisted by L. W. Davis, F. Archibald, and others at Beverly. Scientists from a number of institutions, including Massachusetts Institute of Technology, Columbia University, and the Bureau of Standards also assisted in the metal program of Alexander. During the expansion of operations, minor changes were made in the process but the charge remained a mixture of calcium hydride and uranium oxide. For a period the oxide used was UO_2 but in general U_3O_8 seemed to give a better product. If the charge was held at a temperature above 960°C to complete the reaction, the product was usually less pyrophoric, but the pyrophoric nature of the metal was still a source of difficulty in processing. The product at first was supplied to the atomic scientists as pressed and sintered briquettes, then for a time the metal was melted and cast, but the briquettes were later preferred.

The elimination or exclusion of detrimental impurities from the metal obtained by the calcium hydride reduction presented a difficulty for some time, but this problem was eventually taken care of adequately when redistilled calcium and high purity oxide became available and minor changes were made in processing. However, the pyrophoric nature of the metal during the processing and even in the sintered product, which was generally somewhat oxidized, was always to be guarded against. The oxide content of this metal caused low yields when melting and casting procedures were employed.

The Metallurgical Project, with its headquarters at the University of Chicago, had a number of other associated laboratories taking part in the program. When the organization was being set up in February, 1942, F. H. Spedding of Iowa State College was invited to participate in the program and direct the chemical research and development effort at Chicago. In addition, a small program involving metallurgical and chemical investigations was set up in the Chemistry Building of Iowa State College at Ames, Iowa. Fortunately, metallurgical research facilities had been set up in this building a score of years earlier by Anson Hayes who had included physical metallurgy as a part of his research program in applied physical chemistry. Spedding alternated between Ames and Chicago, spending about half of his time at each place. H. A. Wilhelm was connected with the metallurgical phase of the work with Spedding at Ames. In the spring of 1942 others joined in the effort in metallurgy; these included W. H. Keller and C. F. Gray who assisted in the work on metal reduction and on metal casting, respectively.

Processes then in operation at Westinghouse and at Metal Hydrides were producing some metal, but they were posing problems that made early tonnage production of high purity metal appear rather dim. Because of the shortage of metal at the time, the physicists were considering other forms of uranium such as oxide and carbide to serve as the major part of the fuel for the first reactor. Furthermore, very little was known about crucibles and techniques for melting and casting of uranium at this early date. Westinghouse was getting good castings on a small scale by vacuum induction melting of their pressed powder compacts in beryllia ware. But beryllia ware was costly and available only in small sizes, and in many cases the crucibles lasted for only one melt.

New Developments in the Casting and Preparation of Uranium Metal, Mid-1942

Although the Metallurgical Laboratory did not have the primary responsibility for the procurement of uranium, it appeared all important to the success of the program on plutonium that some action be taken on all phases of the metallurgy of uranium from obtaining the ore through purification, production, fabrication, testing, protection, and behavior in use. As a part of this action, uranium metal preparation studies were started at Ames in February, 1942. Later, when small amounts of Westinghouse and Metal Hydrides metal became available, melting and casting of uranium were also investigated at Ames.

By mid-June of 1942 it had been clearly demonstrated by Gray, Spedding, and Wilhelm (*16*) that uranium metal could be vacuum-induction melted and cast in graphite without excessive amounts of carbon pickup. When sintered briquettes from Alexander were heated in a graphite crucible to well above the melting point of uranium, liquid metal flowed from the briquettes and collected in a graphite mold to form a massive piece of metal. Most of the oxide in the briquettes remained behind as a spongy mass. Marden's experience with casting of uranium in graphite was unfavorable; however, the results at Ames on the use of graphite as an acceptable material for both the melting and casting of uranium metal were confirmed in tests by Creutz then at the Metallurgical Laboratory and later by John Chipman at MIT.

Since graphite was available in large sizes for making crucibles and it could also be heated inductively in a vacuum, it was considered that the development of large scale melting and casting of uranium metal would be rather straightforward; all that was needed then was a supply of uranium metal sufficient to do the large scale casting.

The uranium melting and casting at Ames during most of the remainder of 1942 was done by placing the metal charge on a graphite grill in the bottom of a graphite crucible which was seated on a graphite mold. This graphite crucible-mold unit was induction heated under a vacuum in a large silica tube or thimble with pulverized refractory firebrick as thermal insulation between the graphite and wall of the silica tube. The upper end of the silica tube was fitted with a special

vacuum head, and a vacuum was maintained during heating and cooling of the casting unit. The entire assembly was supported in a vertical position with the induction coil placed around the outside of the silica tube. The temperature in the crucible during heating was followed by making optical pyrometer observations through a window in the vacuum head. After completion of a casting, the assembly was cooled to room temperature and then dismantled to recover the ingot. Oxide film, skulls, and oxide sponge were generally retained by the graphite grill as the liquid metal flowed from the crucible to the mold which was at a temperature near the melting point of uranium. This method of melting and casting was referred to as "drip casting."

Late in the summer of 1942 work was started on setting up in the Metallurgy wing at MIT, a foundry for melting and casting uranium powder produced at the Metal Hydrides plant. Later in the year when this foundry got into operation, metal powder was packed in one-gallon cans, refrigerated in dry ice and trucked from Beverly to MIT for processing. Some of the powder was vacuum induction melted in graphite crucibles and cast into bars and rods, some was merely pressed in the form of cakes ($1'' \times 1'' \times {}^1/_2''$) and then shipped back to Beverly for sintering before delivery to the Metallurgical Laboratory in Chicago. The metal in the form of the sintered cakes, known as "Doan's Yeast Cakes," was somewhat pyrophoric, and many of these cakes were later returned to MIT for melting and casting.

In the uranium metal preparation studies at Ames, the early work was done with uranium oxide, the most commonly available source of uranium at the time. The carbon reduction method employed by Moissan was repeated with variations employing induction heating, and although massive chunks of metal were obtained, the metal always contained sufficient carbon to make it quite brittle. Other reductants such as hydrogen, magnesium, and aluminum were tried. The hydrogen did not reduce the dioxide at the highest temperatures used; aluminum reductions at temperatures near the boiling point of aluminum gave a somewhat solid mass of uranium contaminated with aluminum and aluminum oxide. None of these experiments gave evidence of a desirable process for uranium metal. This program at Ames continued in an effort to investigate or develop processes other than those in use at Metal Hydrides and at Westinghouse.

In the summer of 1942 small amounts of uranium tetrafluoride became available to the Metallurgical Project. This material was being considered at Chicago as a possible fuel material for the first reactor and was being demonstrated in the form of briquettes weighing a few hundred grams each. F. H. Spedding brought one of the briquettes to Ames where it was repulverized for use in metal preparation studies. One of the first experiments was to mix granular calcium in excess with 170 g of uranium tetrafluoride and place the mixture in an iron crucible which was then closed and heated in a vacuum until ignition of the charge took place. On opening the crucible, it was found that the products of the reaction had fused by the heat generated during the reaction, and the metal had agglomerated into relatively large pieces that were easily separated from the slag, giving a massive uranium metal yield of more than 60 per cent.

Results of experiments by Keller, Spedding, and Wilhelm on the reduction of UF_4 with calcium were reported to the Metallurgical Project early in August, 1942. Although this reduction gave the type of product desired, it was obvious that much more work was needed to perfect the process. The use of a mixture of magnesium and the tetrafluoride was also being considered as a possible charge variation for preparing uranium metal by this method, which merely required preheating or fuse-igniting the charge in a closed vessel. Although cost, purity, and supply favored magnesium, the urgency of the metal situation at the time and the many unknown factors involved in bomb type reductions required that the process employing calcium, which is thermodynamically more favorable than magnesium for reductions and which had given positive results, be developed first and at as early a date as possible. Therefore, for several weeks essentially all of the very limited supply of uranium tetrafluoride available to Iowa State College at Ames was employed in calcium reduction studies.

Also in August, 1942, C. J. Rodden, working independently at the National Bureau of Standards, made experimental reductions of uranium tetrafluoride with calcium and obtained results similar to those at Ames.

On August 20, 1942, workers at Brush Beryllium Company (*17*), at the suggestion of Szilard and Creutz, tried the preparation of uranium metal by a method similar to that used for preparing beryllium metal. In the operation, alternate additions of magnesium metal and uranium tetrafluoride were charged into a heated graphite crucible, and the heating continued under an atmosphere of argon to temperatures well above the melting point of uranium. The charge was held at these high temperatures for a period in an effort to get segregation of the metal and slag phases. Although this work on the development of an open-crucible post-heat process employing a charge of alternate layers of magnesium and UF_4 was continued for several months, metal yields and quality were such that the process never became important as a source of metal.

There were, then, by early fall of 1942 at least six laboratories working to improve or develop processes for preparing uranium metal. These were Westinghouse, Metal Hydrides, Iowa State College, The Bureau of Standards, Brush Beryllium, and Brown University, where C. A. Kraus (*18*) was working on the sodium reduction of uranium chlorides, especially UCl_4 and UCl_3. The work of Kraus was continued for the purpose of developing a process for very pure metal in small quantities, but the sodium reduction of chloride was never operated on a commercial scale.

Fortunately, certain earlier developments in related atomic energy and other projects facilitated the work at Ames on the calcium-uranuim tetrafluoride bomb process. The availability and purity of the reactants employed would determine largely the expansion of the operation and the purity of the uranium metal produced by the bomb process.

The Bureau of Standards had already solved, to a large extent, the calcium metal purity problem which had plagued the earlier work on uranium metal pro-

duction at Metal Hydrides. Although the cost of distilled calcium was disturbing at the time, the urgency for uranium metal left the production capacity for calcium as essentially the major concern.

Prior to World War II there was no commercial production of calcium in the United States to supply the needs for that metal in various metallurgical operations. The consumption of calcium metal in this country which amounted to upwards of 42,000 pounds per year depended essentially on importations from France. A few days after World War II started in 1939, Electromet began the design of an electrolytic calcium process for the Union Carbide plant at Sault Ste. Marie, Michigan. Under the direction of G. D. Bagley, the plant was set up and producing metal sufficient for the needs of this country in 1940 when the supply from France was abruptly cut off by the war. In the summer of 1942 this plant was in the process of expanding further, with calcium distillation equipment being set up to supply purified calcium for use in the atomic project.

Furthermore, considerable work had been done on the preparation of UF_4 as an intermediate in the production of UF_6 for studies on one of the uranium isotope separation projects. A dry process for UF_4 had been developed at Johns Hopkins University. In the summer of 1942 DuPont at Penns Grove, New Jersey, and Harshaw Chemical in Cleveland were in the process of setting up larger scale production operations for the UF_4 from high purity UO_2. Westinghouse had found that UF_4 as well as their sunlight-dependent KUF_5, could be employed in their electrolytic process. Large scale operations for high purity UF_4 had, therefore, been planned and were definitely well along toward realization.

The Calcium-UF_4 Process Expands, Late 1942

As materials which were still very limited in supply became available to the laboratory at Iowa State College, the many variables connected with design of reduction bomb, method of ignition of charge, refractory liner, particle sizes of reactants, proportions of the reactants, sizes of charges, atmosphere in the bomb, and other variables affecting yield and quality of the metal were hurriedly investigated to determine somewhat optimum conditions for production. Test reductions through most of the month of August, 1942, were made with charges containing not more than 200 g of UF_4 each, but by mid-September sufficient fluoride was on hand to increase experimental charges to two or three kilograms of UF_4. Yields of metal for these larger charges were then averaging better than 90% in one massive piece of metal, referred to as a "biscuit."

In late September some of these biscuits that had been obtained in reduction experiments at Ames were cast into one ingot by melting and casting in graphite by the "drip casting" method described earlier. The ingot weighed eleven pounds and was 2 in. in diameter and approximately $5^1/_8$ in. in length. This ingot was taken to Chicago and given to Spedding who placed it on the desk of A. H. Compton. Compton handled the ingot carefully and, with a detectable twinkle in his eye, remarked, "I'll wager there is a big shrinkage cavity inside." The ingot was subsequently cropped, and the resulting billet cut to give two solid cylinders each about $2^1/_4$ in. in height. There was not the slightest indication of an internal void. E. C. Creutz made a quick density determination of one section and reported a value of 19.04 g/cc.

After this event the experimental operations at Ames on metal preparation were stepped up rapidly. As more raw materials became available, a production crew was organized and by October 10 metal was being produced at a rate of 100 pounds per week. R. L. Doan, director of the Metallurgical Laboratory, assisted the Ames group by supplying funds and materials and by setting up proper contracts to get metal pilot plant operations started on the campus at Iowa State. A somewhat dilapidated, one story wooden building on the campus was selected for the future pilot plant. This building was a "temporary" building left over from World War I. It had had various uses in the meantime, having served as a gymnasium for women at one time, and when taken over for the metal pilot plant it was being used as a combination garage and pop-corn laboratory.

While the conversion of the building and the installation of its equipment were in progress, pilot plant production of uranium was continued in the laboratories of the chemistry building. More than two tons of uranium ingots were produced in the chemistry building and were shipped to Chicago by the end of November, 1942. The ingots were being cast as solid cylinders about $2^1/_4$ in. in diameter. These ingots were cut into 2- to 3-in. long sections that were referred to as "eggs."

The chain reacting pile under the west stands at Stagg Field at the University of Chicago contained about equal amounts of metal as eggs, etc., from each of the three producers, Westinghouse, Iowa State College, and Metal Hydrides, and a number of tons of pressed cylinders, or eggs, of uranium dioxide when it reached criticality on December 2, 1942.

The supply of good quality calcium metal for uranium production, although sufficient through most of 1942, was definitely inadequate in view of proposed future requirements for uranium metal. By late 1942, production of UF_4 and the preparation of uranium by calcium reduction of UF_4 were sufficiently established to warrant diverting calcium from the Metal Hydrides process to the calcium-UF_4 bomb process at Ames. Since good quality metal had been assured at a lower cost by the latter process, the preparation of virgin uranium metal by Metal Hydrides, Inc., for the Metallurgical Project was then curtailed. To meet possible future calcium metal requirements for uranium metal production, Union Carbide late in 1942 was requested to design a much larger calcium metal production plant. Since Westinghouse did not employ calcium metal, their uranium production continued to expand into the year 1943.

Important Developments Related to Uranium Metal Production

The metal production outlook was definitely much brighter by the end of 1942. Supplies that were essential to producing good metal in quantity at an early date had been explored and, where necessary, production properly expedited by Compton, Doan, Hilberry,

and others in the interest of the Metallurgical Project. Let us consider for the moment the supply of uranium ore, the treatment of ore, the preparation of high purity oxide, and the conversion of dioxide to fluoride. Each of these areas is all-important to metal production, and the developments connected with each of them represent much concentrated effort by scientists concerned. Each area has an interesting history in itself, but only brief references to some phases can be included here.

Fortunately radium had been in demand for a number of years, and, as a result, uranium mining operations which were of interest to the uranium metal program in America had been developed to some extent in Africa and in Canada. Furthermore, some very impure uranium oxide was available in the U. S. as a by-product of vanadium production. The mining operation of most importance in the early development days was that of the Canadian Radium and Uranium Company. This company obtained its ore from the Great Bear Lake area and had a relatively large stockpile of crude (92%) uranium oxide at Port Hope, Canada.

Some operations were hurriedly set up to improve the purity of this crude oxide on a large scale by ordinary chemical techniques; however, Spedding suggested to Compton that an extraction purification involving ether-uranyl nitrate be explored as a commercial possibility. The chemistry section of the Metallurgical Laboratory began work on this problem, and by early April, 1942, adequate data had been obtained by the group under George Boyd to begin the design of a process for purification.

One hundred years earlier, in the year 1842, Peligot (*19*) had made use of the solubility of uranyl nitrate in ether in a purification scheme. More recently laboratory scale purification of uranium by ether extractions had been employed at Columbia University by H. L. Anderson in 1939 for removing daughter products and other impurities, and at the Bureau of Standards by J. I. Hoffman in 1941 for separating good purity uranium from a number of other elements.

The Mallinckrodt Chemical Works at St. Louis was approached by Compton and Spedding with the problem of putting an ether purification process for uranium into large scale production. With the operating conditions set up by Boyd's group, the Mallinckrodt chemists and engineers made further refinement studies and built the large scale purification plant. The ether extraction purification was proposed to H. V. Farr and John Ruhoff of Mallinckrodt on April 17, 1942, (*20*) and by early that July the plant had been built and was turning out one ton of high purity oxide per day.

All crude uranium oxide concentrate prepared at Port Hope and at The Linde Air Products Company plant at Tonawanda, New York, where most of the domestic supply was processed in the early years of the program, was then shipped to Mallinckrodt for purification. Shipments of the oxide from Canada to Mallinckrodt in the critical production period of 1942 were often made by air. Mallinckrodt was the sole supplier of ether purified UO_2 for a number of months.

Production of UF_4, as mentioned above, was set up at DuPont and Harshaw late in the summer of 1942. Mallinckrodt entered UF_4 production late in 1942. The UF_4, known as "green salt," was then available from three producers, all using Mallinckrodt dioxide.

Equally important to the metal production program were studies and operations bearing on the fabrication, protection, and use of the uranium metal. An expanded historical treatment could include much material on the great amount of effort that went into these phases of the total metal story. Among those connected with these early developments one recalls the important work of E. C. Creutz, J. M. Simmons, John Howe, D. H. Gurinsky, and others at the Metallurgical Laboratory; of John Chipman, Frank Foote, and Al Kaufmann of MIT; of H. W. Russell and associates at Battelle; and of J. G. Thompson of the Bureau of Standards.

In the early days of metal development, certain investigations were hurriedly made in an effort to gain an adequate working knowledge of the behavior of this essentially new metal. Many scientists at laboratories associated with the Plutonium Project participated in this effort in studies of alloys, of chemical reactivity, of physical properties, and of other characteristics of uranium metal. Although these scientists were not generally recognized as being involved in the preparation of the metal, information which they supplied was often of valuable assistance to those directly confronted with the problems associated with the development of metal production.

A very important activity on which the entire uranium metal program was quite dependent was that of the analysts. New and more sensitive methods of analyses for impurities in uranium had to be developed under pressure of the urgent need for control of metal quality. Among the many who contributed much to this phase of the metal program were C. J. Rodden and B. F. Scribner at the Bureau of Standards, N. H. Furman at Princeton, H. A. Potratz and George Boyd at the Metallurgical Laboratory, and J. C. Warf and V. A. Fassel at Iowa State.

The government agencies or committees that operated to assist in setting up and in furnishing some financial support to earlier phases of the atomic project influenced directly only to a small degree the course of the history of the development of uranium metal in America. The major impellent specifically to furthering uranium metal production and process development for the atomic project came largely out of the requirements of the plutonium enterprise which was initiated by Compton in late December, 1941. This program became a part of the over-all program which was administered largely by L. J. Briggs, J. B. Conant, and V. Bush of the OSRD for a period after the December, 1941, reorganization of the administration for atomic matters. The OSRD through the S-I Section and its successor, the S-I Executive Committee which was established in May, 1942, carried most of the administrative responsibility during the early development work on processes leading to large scale metal production.

The Manhattan District of U. S. Army Engineers which was established in August, 1942, with L. R. Groves in charge after September 17, gradually worked into the Project. By January, 1943, the procurement of raw materials, equipment, and other facilities for

meeting metal requirements for research, development, and production was essentially the responsibility of John Ruhoff, then of the Army Engineers. On May 1, 1943, the OSDR turned over completely the administration of the uranium project to the Manhattan District.

Development and Industrialization of the Ames Uranium Process

The pilot plant operation that was set up at Iowa State College in the latter part of 1942 and early 1943 served a number of purposes. It operated as a production plant to supply the much-needed uranium metal for reactors at Chicago, Oak Ridge, and Hanford. It served as an experimental laboratory for studies leading to improvements in the process. At the same time, it was a working example for industrial personnel who were planning to adopt the process to visit and learn firsthand the details connected with the bomb production of uranium metal. Frequent visits to the college campus at Ames were made by scientists and engineers from Electromet, DuPont, and Mallinckrodt to get design and operational details connected with this process for use in planning their industrial uranium metal plants.

It was pointed out above that, although development of a metal production process at Ames was originally based on employment of calcium as reductant, the use of magnesium for the reduction of UF_4 in the bomb process would have certain advantages. Experiments at Ames to determine the possibilities of magnesium were renewed in early November after production by the calcium-uranium tetrafluoride process was in a fair state of development. Earlier exploratory tests had demonstrated that the heat developed by the reaction employing magnesium metal was not sufficient to fuse the products of the reaction when the mixed charge of granular magnesium and finely-ground uranium tetrafluoride at room temperature was ignited by means of a fuse. The renewed effort on the use of magnesium was then directed toward adding heat to the mixture either by preheating the charged bomb in a heat soaking pit before ignition or by adding to the charge materials that would give an auxiliary reaction to serve as a "thermal booster."

On November 10, 1942, a yield of 80 per cent of theoretical for the UF_4 mixed with magnesium was obtained as massive metal by preheating the bomb before ignition. Although the thermal booster also gave equivalent results in the early tests, most attention was given to the development of the preheating process for the magnesium reduction of uranium tetrafluoride. Because of the lower heat of reaction obtained with magnesium and its lower boiling point, conditions for the magnesium reduction were more critical than for the calcium reduction. For the efficient use of magnesium in the bomb process, much further development was required.

By December, 1942, the reduction operation which was still dependent on the use of calcium metal was moved into the pilot plant building, then known on the campus as the "Physical Chemistry Annex." Because of the more complicated machinery, such as induction furnaces, vacuum systems, etc., that had to be set up for metal casting at the Annex, the casting operation was continued with the equipment in the chemistry building until early in 1943. Larger casting equipment was employed at the Annex and the drip casting method was replaced by a crucible with a valve for pouring the metal.

As bomb reduction techniques and the quality of materials improved, the yields and quality of metal by the magnesium process also improved to such an extent that the entire uranium metal production at Ames after January, 1943, employed only the magnesium reduction of uranium tetrafluoride (*21*). The process, as established, employed a steel bomb that was lined with a powdered inert refractory. The mixed charge was placed in the lined bomb; the charge was covered with more of the refractory, and the bomb closed with a blind flange (see Fig. 2). This charged bomb was placed in a heat soaking pit maintained at such a temperature that the charge was heated to a point at which spontaneous ignition took place. The reaction that followed developed sufficient additional heat to cause the products to fuse, allowing the dense liquid uranium metal to collect in the bottom part of the bomb with the liquid magnesium fluoride slag on top. The bomb was then allowed to cool and the solidified metal removed as essentially one large mass, or biscuit.

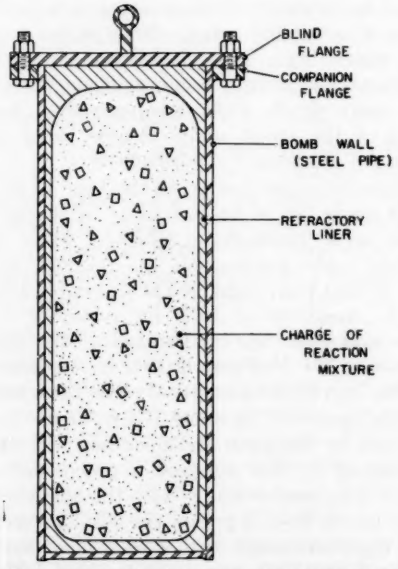

Figure 2. Sketch representing lined, charged, and closed bomb ready for placing in heat soaking pit.

The biscuit weight varied with the size of bomb employed. Bombs made from 10-in. diameter steel pipe, about $3^1/_2$ ft in length, gave biscuits that weighed around 125 lb each. However, most of the metal produced at Ames was made in 6-in. diameter bombs, 3 ft in length, and these gave biscuits weighing about 42 lb each. The biscuits were delivered to the casting room where they were vacuum induction melted in graphite and poured by a valve mechanism into a relatively cold graphite mold.

By the time the industrial concerns were ready to start production by the Ames bomb process, factors influencing yield and quality of metal by the magnesium-UF_4 process were fairly well understood and

under control. Therefore, only magnesium was employed in the bomb reduction of uranium tetrachloride at the new industrial plants. Electromet was the first of the new plants to prepare an ingot of metal, and this was from their reduction and casting operation at Niagara Falls in July, 1943. G. C. Bagley, R. Briney, and E. C. Forbes were in charge of operations there. The Mallinckrodt metal plant, with H. V. Farr, C. D. Harrington, and H. E. Thayer in charge, came into production a few days later, also in July, 1943, and DuPont metal production followed. As these industrial plants entered the metal picture and increased their production, the production operations at Ames were gradually cut back with testing and further process development work remaining as the major objectives.

The Westinghouse production had supplied metal by the electrolytic process before and during the development days of the Ames process. The established industrial production by the magnesium-UF_4 process, however, was adequate to meet the requirements of the Metallurgical Project; so Westinghouse discontinued their operations in the fall of 1943. In the interval covering about one and one-half years of operation, Westinghouse had produced about 65 tons of good quality uranium metal for the atomic energy program.

The industrial plant operations that were set up at Mallinckrodt, Electromet, and DuPont in 1943 were patterned closely after the operations as carried out in the small uranium production plant on the campus of Iowa State College. The major variations were found in the metal casting equipment at Electromet and Mallinckrodt. Both employed a type of casting unit that consisted of a large steel vacuum tub inside of which the induction coil was centrally positioned. The melting operation was carried out in a graphite crucible mounted inside the coil and thermally and electrically insulated from it. The graphite melting crucible was fitted with a pouring hole that during the heating was closed by a valve rod or mechanism. Graphite molds were mounted in the vacuum tub below the crucible; these could be maneuvered into position under the pouring hole. In making castings the metal biscuits were charged into the graphite melting crucible which was then covered, except for a sight hole for visual inspection and optical pyrometer measurements. A large steel cover, which was fitted with windows for observing operations inside the tub, was swung into place and vacuum sealed to the tub by means of a gasket. A vacuum was then developed and the power turned on. The metal was heated to above its melting point and subsequently poured into the graphite molds.

Through the latter part of 1943 and most of 1944, virgin uranium metal was being produced in America at Ames, at Mallinckrodt, at Electromet, and at DuPont. The ingots of uranium that were cast from biscuit metal during this period were generally about $4^1/_4$ in. in diameter and varied in length from 13 in. upward. These ingots were shipped from the metal production plants to commercial fabricators where they were extruded or rolled to rods slightly less than $1^1/_2$ in. in diameter. These rods were then surface machined to the desired diameter and then cut to give slugs a few inches in length. The finished slugs were inspected, canned, tested, and introduced into the reactors at Hanford.

As a result of the fabrication operations, many tons of uranium metal turnings, chips, and rod ends had been produced and were piling up. A process was desired for recovering these by converting them to ingot metal without reprocessing chemically; this would boost the available ingot supply materially. Such a process for the large scale recovery of uranium metal chips and turnings was developed at Ames and put into operation in early 1944.

Uranium operations in the Physical Chemistry Annex (Fig. 3) were discontinued on August 5, 1945. Metal recovery, ingot production directly from the bomb (*21*) which by-passed remelting and gave low carbon metal, development work on biscuit production, and development of a rod casting method (*21*) designed to bypass ingot processing were the main phases of the work in this building during the last few months of World War II. Earlier, when the major metal production effort in America depended on processing at Ames, the plant was kept in operation continuously 24 hours per day for 7 days each week. Over one thousand tons of uranium metal ingots were produced and shipped from this plant in the critical years. Following the uranium production, the building was used to produce thorium metal and later, when operations were moved to other sites, the building became less active than it was radioactive; so, in 1953 it was torn down with some salvaged, some burned, and some buried. This building disposal was performed as somewhat of a public relations measure, since the building was close to the college dairy industry building and the women's dormitories.

Figure 3. Physical Chemistry Annex on the campus of Iowa State College, Ames, Iowa. This was the first large-scale uranium metal production plant in America.

Shortly after World War II, the turnings recovery operation was moved from Ames to Metal Hydrides, and at Electromet and DuPont metal production was terminated. Mallinckrodt Chemical Works in St. Louis was the only plant that continued to produce virgin uranium metal. Mallinckrodt set up operations for complete processing of uranium starting with ore concentrates and carrying through purification of the nitrate, preparation of UO_2 and UF_4, metal biscuit production, and casting of uranium ingots. The Manhattan District continued to administer the atomic project until organization of the U. S. A. E. C. which was established by Congress in 1946.

Under the Atomic Energy Commission, an entirely new uranium production plant was built for Mallinckrodt. Although the same metal reduction process was employed, many of the operations were mechanized in this new plant in St. Louis. In 1952 another large plant for complete operations, from treatment of uranium ores to metal production through fabrication, was set up by the U. S. A. E. C. at Fernald, Ohio, about 30 miles from Cincinnati. This plant was patterned after the operations then at Mallinckrodt, except that the metal fabrication and turnings recovery operations were added. A company designated as the National Lead Co. of Ohio operates this plant. Mallinckrodt now has an entirely new and expanded operation at the Weldon Spring plant, just west of St. Louis. A few industrial concerns in America are now producing uranium metal independently of the U. S. A. E. C.-sponsored operation; these concerns produce the metal by essentially the same process but on a relatively small scale.

In 1959 the principal reaction and conditions used in producing uranium metal in America are essentially the same as developed at Iowa State College in the early 1940's. At the Fernald plant minor processing changes include mechanization, sizes of charges, casting equipment, and refractory bomb liner material. Also, the massive piece of metal obtained from the reduction bomb was called a "biscuit" in earlier days, but the industrial plants today refer to this piece of metal as a "derby."

In the early metal production days at Ames the refractory used to line the bomb was a high fired ("dead burnt") high calcium lime specially prepared by the St. Genevieve Lime Co. of St. Genevieve, Missouri. When properly prepared and handled, this material was very satisfactory; however, due largely to the relatively small scale of this operation there was some variation in the quality of batches by the time they were ready for use. A lime with a high loss of weight on ignition was very undesirable, especially for the magnesium reductions. Improperly prepared liner material would sometimes fail at spots on the bomb wall during the fast heating that followed ignition of the charge. A failure allowed the hot reaction products and magnesium vapor to react with the steel, pitting the wall and sometimes causing a burnout. Failure of the steel wall was evidenced by a roaring white hot jet of burning magnesium vapor that extended a number of feet from the bomb.[1]

[1] At Ames an experimental production bomb failure during the night shift swung one wall of the pilot plant building (Physical Chemistry Annex) several feet out of position. The workmen on the shift went outside and set the wall back in position and metal production went on practically uninterrupted.

In another incident, after the Army had stationed a uniformed representative, Major H. A. Savigny, at the Ames plant to serve essentially as expediter, a bomb failure caused him to receive a few slag burns on his clothing. At the plant there was consideration for giving the major a decoration for activity other than in the line of duty. However, the decoration was not awarded since there was evidence of retreating at the peak of activity; the seat of his pants showed the most effects of the incident.

Late in 1943, Electromet prepared a linear material by electric arc fusion of dolomitic oxide. This material which was quite uniform and highly satisfactory was adopted and used exclusively as the liner material for a number of years. In most of the production operations today magnesium fluoride, reclaimed from the slag, is used as the bomb liner material.

The chief innovation in industrial production has recently been put into operation at the Weldon Spring plant (*22*). Here the bomb is of such size and shape that a single biscuit of about 3000 lb of metal per charge is produced in the form of a cylinder 18 in. in diameter by 18 in. in length. This cylinder is recovered from the bomb and freed of surface and embedded slag by machining; it is then gamma extruded into the form of a seven-inch diameter billet for rolling to rod. The 3000-pound cylinder or biscuit formed in the bomb is referred to as a "dingot" (from direct ingot). As in the "direct pour" process (*21*), remelting in graphite is bypassed and consequently the carbon in the metal is very low.

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J. A. Campbell
Harvey Mudd College
Claremont, California

Preparation for Graduate Work in Chemistry

A conference report

It is impossible to say exactly where the professional training of a chemist begins, but the first formal course of most chemists is in high school. Such courses vary (especially as a function of the education of the teacher) from those given without laboratory by a teacher with no prior training in chemistry to those which are the equal of the best college first-year courses. College curricula vary in similar fashion from minimal two- or three-year programs given with scant chemical insight and even less modern equipment to programs of such strength that an appreciable number of their graduates proceed to the Ph.D. in two further years. Unfortunately variance in the caliber of graduate school education is similar.

There is, however, general agreement on the virtues an entering graduate student should have: he should be conversant with the language of chemistry, have an acquaintance with the chemical literature and the means of using it, be skilled in problem-solving techniques (for both quantitative and non-quantitative problems), have a good background in physics and mathematics, have a strong liberal arts education, be capable of making intelligent choices and experimental designs especially in chemistry, be able to impart information to others, be able to read and learn without formal courses.

Such a partial list of virtues leads immediately to the recognition that only seldom can all be achieved, and the ones which are achieved will seldom be achieved equally. Most of us operate under a "constant volume" condition. Increased emphasis on some new point in the curriculum means decreased emphasis elsewhere. Attainment of some of the goals inevitably means partial sacrifice of some of the others. But even in a "constant volume" system change is possible and many functions can be maximized simultaneously. Which functions maximize will vary with the goals of the experimentalist and the nature of the system.

One person summarized the goals, "You can't possibly teach a student all the facts that he's going to know, but if you can teach him to have self-confidence in learning how to study his problems and to go out and get the facts, and give him enough perspective as to where these facts are, I think you're giving the best sort of training you can give."

Let us then make the following assumptions: (1) Ideal preparation for graduate work in chemistry will vary with the student, with the graduate school be is to attend, and with the interests of the staff in his undergraduate college; there is no ideal curriculum either total or chemical. As one conferee put it, "I believe pretty much in anarchy, where those who are not willing to take it on their own conscience should suffer the consequences." (2) A high degree of autonomy and experimentation in programs should be encouraged not only because of the inevitable expansion in chemical ideas, but also because of the individual nature of the student and his college. (3) There are at least two different but not mutually exclusive problems in educating undergraduate chemistry majors—professional training and preparation for graduate work. The approved curriculum suggestions of the Committee on Professional Training are concerned with professional training, and the Committee has consistently emphasized that the suggestions do not necessarily constitute the best preparation for graduate work. (4) This paper will adhere closely to the title—Preparation for Graduate Work in Chemistry—and will not deal, except incidentally, with chemistry courses for those of other interests. (5) "Units" of credit are defined as semester hours: roughly, $^1/_{125}$ of the total graduation requirement, or $^1/_{16}$ of a semester load.

A conference on this topic was first suggested at the 1958 Chicago Meeting of the American Chemical Society to the Committee on the Teaching of Chemistry of the Division of Chemical Education. Considerable experimentation is now going on in various undergraduate and graduate curricula and it seemed wise to discuss these and other trends. A proposal for such a conference to consist of some twenty chemists known for their interest in the problem and representing both undergraduate and/or graduate points of view was submitted to the National Science Foundation which granted the support for a conference to be held at Harvey Mudd College.

The following men attended the conference: R. A. Beebe, Amherst; J. A. Campbell, Harvey Mudd; L. B. Clapp, Brown; L. N. Ferguson, Howard; E. L. Haenisch, Wabash; G. P. Haight, Swarthmore; L. P. Hammett, Columbia; C. H. Hansch, Pomona; R. E. Henze, American Chemical Society; C. G. Niemann, California Institute of Technology; K. S. Pitzer, U. C. Berkeley; A. Roe, North Carolina; A. F. Scott, Reed; M. J. Sienko, Cornell; L. E. Steiner, Oberlin; L. E. Strong, Earlham; E. H. Swift, California Institute of Technology; H. Taube, Chicago; and J. E. Willard, Wisconsin.

No resolutions were passed but this paper presents a general consensus of the discussions and conclusions of the conferees. The paper is phrased in direct English, even though it is a conference report, in order to avoid the continual statement, "The conferees felt—." Each conferee has seen this report prior to publication. While each might differ in the emphasis he would place on the various points and, perhaps, some would not support all the points, there is general agreement on those outlined here.

The High School Background

Student backgrounds upon admission to college will always vary enormously, but there is already evidence that a large number are coming to college with better chemical educations than formerly. This effect will almost certainly increase, partly because of the higher selectivity in the majority of colleges and partly because of the mass efforts under way by the National Science Foundation, the Ford Foundation, and many other groups to encourage the high school teacher to undertake serious new study of his subject from a professional point of view. This is important not only in chemistry but in physics and mathematics. Twenty years ago very few colleges had freshmen in calculus courses, now many do—and more soon will. Admission with advanced standing is becoming common, with students presenting one or more courses of genuine college caliber, but taken in high school. Many colleges are opening their courses to local students who qualify even while they are still in the high school, with the colleges giving full credit while the high school releases the student part time to do this work.

Colleges recognize these changes in various ways. They may give entering students college credit on the basis of the high school record only. (Most colleges give full credit for a "5" on the Advanced Standing Test, many do for a "4," and some give full credit (or else one semester of advanced credit) for a "3.") Many other colleges use their own tests to place students in the second-year course, in the second semester of the regular course, or in special sections of the first-year course. This may involve only advanced placement or it may involve granting credit by examination. Regardless of the quality of performance on examinations, few high school graduates have had laboratory backgrounds comparable to college courses.

The First Year of College

Some colleges let potential chemists take chemistry, physics, and mathematics during the first year, but many restrict the students to two. Common arguments for two science courses are: all students should have academic experience in several fields before they commit themselves to a major, three sciences are too heavy a load for most entering freshmen, elementary courses should be taken in the first two years (junior and senior science majors in elementary economics are in the wrong place). Three courses are defended as: allowing the highly motivated science student to begin immediately with subjects in which he is interested, allowing the early introduction of higher chemistry courses (e.g., physical chemistry) based on physics and mathematics, letting the science student take his humanities and social sciences when his greater maturity will let him get more out of them. "Answers" are of course available to the merits expressed by each side, yet there is little question but that this decision has a major bearing on the chemistry curriculum, particularly on the place in it of physical chemistry and chemical problems requiring calculus.

College Mathematics and Physics

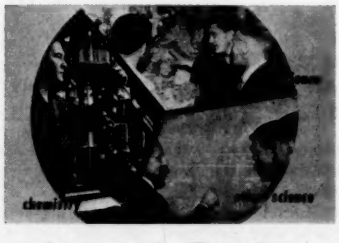
Unless chemistry is to be fragmented, e.g., into mathematical and non-mathematical education, a reasonable background in both mathematics and physics will continue to be expected of all chemists entering graduate schools. The minimum mathematics should include ideas from calculus, analytic geometry, partial differentiation, differential equations, and series. Sufficient trigonometry, if missed in high school, can be given in two weeks. Actual mathematics "requirements" in the schools of those present at the conference varied from 8 to 16 hours. A principal variable is the willingness of the mathematics department to establish a "service" course for the science majors or to adapt its own sequence with their needs in view. This adaptation has been very successful in places where a single mathematics sequence is given but in such a fashion that one year (about 8 units) gives a suitable minimum background for chemists and two years (12 to 16 units) a very good background indeed. The physicists and mathematicians then continue, in further courses, to pick up the material covered in many other schools in the first two years, but with the advantage that the more mature students now do this faster and more thoroughly, so that there is no loss but a gain. Students with strong interests in theoretical chemistry also continue their mathematics for at least another semester. Most will then add another year in graduate school. The goal of a mathematics sequence might be defined as "achieving the comprehension to do the most work with the least number of operations, not with a high speed computer, but with slow speed students."

Physics "requirements" tend to be lower than mathematics requirements but the range, 8–16 units, is the same. Again the second physics course is needed more by the chemist with a quantitative, theoretical bent. Courses in "modern physics" are often less worthwhile than those in analytical mechanics and electricity and magnetism, but the principle differentiation appears to lie in the amount of mathematics used in the physics, large use giving the better course.

The First Year Chemistry Course

More variation in emphasis is found in first-year courses than in any other. Not only is there the common question of a single course, versus multiple ones designed for different "needs" (i.e., chemists, engineers,

—The cover—



The cover photographs suggest that the undergraduate chemist should cut his pie into thirds. This is a pictorial representation of the conclusion of the conference here reported: The optimum program allows for one-third of his time to be spent on chemistry, one-third on mathematics and related sciences, and one-third on the humanities, languages and other non-science courses.

Acknowledgments are due to Mr. Rodney Williams and the public relations staff of the College of Wooster for the picture of the chemistry student engaged in a senior research problem. Similar thanks should go to Mr. Zaner Faust of the news bureau of Harvey Mudd College for the two views of students and faculty at work in other areas.

liberal arts, home economics, nursing) but even in single course institutions the emphasis may be general chemistry, organic chemistry, or analytical chemistry, with amounts of physical introduced varying from a treatment of integration of simple rate equations to a statement of the gas laws.

The syllabus of this course does not, of itself, determine the worth of the course. Much more important is that it be treated as one of the most, if not the most, important course in the department; that it be taught by a professional staff enthusiastic over whatever the content is; and, most importantly, that it deal with intellectual and experimental areas new to the students, rather than covering those already introduced in high school. It should not be remedial, but insist on an adequate total high school background.

It is more economical of staff and student time to set entrance requirements for the first-year course, than to cut down on the laboratory until the poorly prepared students drop out. The laboratory is one of the more important features of the course. Or as one put it, "There are two ways to learn chemistry—in the laboratory or by teaching it." The present low status of first-year and other laboratories is due largely to the absence of real experiments. Unfortunately the student usually knows the "answer," follows detailed directions in trying to achieve it experimentally, and only succeeds in confirming his prior belief that the work of others is considerably more accurate than his own. The most successful laboratories seem to be based on the following: A problem or unknown is given to the student; he has at least some hand in designing the experimental approach; he makes continual observations of importance rather than merely noting a final answer; the experiment involves his abilities and comprehension actively; the results are often quantitative and satisfy his idea of attainable accuracy and his own limitations. A small number of intensive experiments is better than a large number covering more chemistry.

The purpose of the first-year course for chemistry majors is at least threefold: to foster and increase the interest and education of those already planning a major in chemistry, to attract those who can do well in this field but had not yet made the decision, and to give those who question their original choice of chemistry as a profession, or may not do well in it if they continue, a full opportunity to make a reasonable decision. No curriculum should be so rigid that the two latter groups are forgotten. You first have to "catch the rabbit to make rabbit stew."

Further Basic Courses in Chemistry

The first-year course varies so much in content that it is not feasible to discuss further courses in a sequential way which will be useful to very many schools. It is generally agreed, however, that the basic requirement for a chemistry major can be accomplished in four, one-year courses (about 32–35 units). Additional advanced courses must be included, but we shall discuss these a little later. But, how does one best make this statement consistent with the growing practice of giving advanced placement or standing to entering students who thus skip the normal first-year course? What should the Committee on Professional Training, for instance, respond to a school which says: "All of our students come in with excellent high school backgrounds. We are, therefore, eliminating our general chemistry course and continuing the analytical, organic, and physical programs. This will free staff time and further enhance the worth of our program."

Currently the students obtaining advanced standing are a small percentage of the total and are demonstrably better educated and capable of acceleration. The loosening of strict requirements they have allowed has been helpful to the colleges, but the question of adapting to the presumed increase in general worth of high school chemistry and science in the near future presents a larger problem. In terms of our "constant volume," however, it seems clear that the new material desirable in the college curriculum will at least keep pace with the possible transfer of general chemistry from the colleges to the high schools. There seems little possibility of decreasing the colleges' course responsibility.

The distribution of material among these courses is pertinent. Let us deal with them under their classical titles.

Analytical Chemistry

One of the largest current shifts in chemistry is from the former emphasis of analytical courses on determining the composition of "synthetic" unknowns, to developing quantitative concepts of chemical equilibrium and the application of physical chemical methods, including instruments, to studying the properties (rather than only the gross composition) of chemical systems.

More and more colleges are deviating widely from the Fresenius scheme of qualitative analysis. They ask rather that their students study the chemistry of a selected set of anions and cations, for instance, and then discover suitable methods for separating them or identifying them in the presence of one another. The emphasis is on the control of concentrations by the student, instead of by the directions; on the mastery of a relatively simple problem whose attack the student plans, rather than the unraveling of a more complex problem using tools provided by others.

Many schools are moving the quantitative analytical course to later years (so that it can build more on the physical). Others are introducing many of the customary quantitative procedures into the first-year course, or other courses, when they are pertinent to the study of the system under consideration. The analysis is, then, normally only part of the solution of the problem under consideration. A few schools have gone so far as to redistribute all of the customary quantitative analysis emphasis among several courses so that no analytical course as such is given.

It may be that the separate course in analytical chemistry has come close to meeting Latimer's statement, "When a course has achieved its goal, it is no longer given as a separate course."

Organic Chemistry

This branch of chemistry seems as well established with as clear boundaries as any field. There is great

interest in the best way of teaching organic and the best place in the curriculum to include it. It is, in the minds of some at least, the most "self-contained" area of chemistry. The conferees spent relatively little time discussing organic but did raise a few questions.

Organic now seems to be the course in which most of the "unit operations" of chemistry are covered. It is also the area in which mechanisms of chemical reactions are usually treated most completely, and in which such topics as optical activity, isomerism, and polymers are discussed. So exclusive is this attention at times that students associate these phenomena solely with systems containing carbon compounds. Would it be wise (it certainly is feasible) to widen the scope of these initial discussions of the above topics to include other systems? Would it be feasible to allow the students more freedom of experimental design in the organic laboratory? Would it be wise to insist on more use of mathematics and quantitative treatments in organic? Would the use of ground glass equipment more than justify the increased initial cost by using time more efficiently and setting reasonable professional standards for the course?

Some discussion, but no conclusions, rose as to the best year for organic. It is used occasionally in the first year, and about equally often in the second and third year. Is there great merit in putting it into the first year since it requires little mathematical background, is new compared to high school courses, and can cover most of the common compounds and most of the fundamental ideas introduced at present in general chemistry? Or should it follow the physical course and build on the kinetics, equilibrium ideas, and thermodynamics presented there?

Physical Chemistry

There are many arguments for placing the physical chemistry course near the end of the curriculum. It can serve as a capstone course covering and synthesizing most of the important ideas introduced in the other courses. It can be the most abstract chemistry course, require the most physics and mathematics, and can utilize a broad chemical background against which to apply it. It can build on intellectual maturity in its theories and technical competence in its laboratories, virtues which may best be gained in other courses. It has the highest laboratory investment and, some say, can be most effectively used if the number of students is not great.

There is considerable agreement, however, that physical chemistry should come as early as possible, consistent with a requisite background in mathematics and physics. Several schools now have the physical course requiring a calculus and physics background in the second year. Many more would do so but for the impossibility of satisfying the mathematical background requirement in their local situation by that time. The main argument for this early treatment is that it provides a more thorough basis for the treatment of organic, analytical, inorganic, and other courses. It also introduces the student to the broad scope of chemical theory and experimental measurement and gives him insight into many problems which otherwise must be treated empirically. The schools that have and are giving physical in the second year seem convinced that it is no more beyond the grasp of second-year students than is organic (though it may give different students difficulty). Thermodynamics is used broadly, but the full treatment postponed, while work on spectroscopy and quantum effects is introduced.

The physical chemistry laboratory is commonly criticized as involving measurements that lead nowhere. Measurements of the viscosity of water, or density, or refractive index, etc., are standard. Techniques and accuracy are primary goals with which few argue, but the worth and validity of the experiments might well be increased if such measurements were used as means to understanding a system. Density or refractive index, for example, may be just as well used for measuring an equilibrium system or the kinetics of a reaction. A smaller number of more sophisticated experiments on more complicated systems may gain more for the students than a wider number of introductions to the available techniques of measurement. A given experiment should not teach one point; it should teach three or four in a connected fashion. Yet the equipment for each experiment should be understandable and the "black box effect" kept to a minimum. Considerable student initiative may be tapped in the physical laboratory by issuing minimal directions.

Inorganic Chemistry

Formerly strong in undergraduate curricula, then lost by the academic wayside, inorganic chemistry is reappearing in an increasing number of curricula. It has been "remarkable that only carbon is featured as being worthy of detailed treatment as descriptive chemistry, when most chemists think it an accomplished fact that there are over 100 elements."

Few, if any, argue that the chemistry curriculum should be divided equally among the known elements and that a chemist "at age 21 should know everything about all the elements." But many of the most interesting new chemicals are "inorganic," and many of the recent advances in chemical bond theory and theoretical chemistry in general have originated in inorganic systems.

At least three solutions are being tried: (1) A full-scale course in inorganic chemistry which scans the periodic table spending most of its time at "the scenic spots," (2) an intensive course concentrating primarily on the non-metals since their chemistry, i.e., kinetics and mechanisms, has been more thoroughly investigated, or (3) assigned reading and student-run seminars in special areas. Such work is most common in the senior year and can thus concentrate strongly on the professional drive most chemists bound for graduate school have at that time and be firmly based on physical chemistry. Courses in inorganic preparations, when given, concentrate on novel methods other than those common in organic.

Some graduate schools have introduced a preliminary exam in inorganic chemistry to be taken by all entering graduate students. Those who fail must take a course or prepare in some other way until they can pass the examination. Other schools have no such

exam but it is widely recognized that graduate students should have more knowledge of inorganic chemistry than most of them do. (Cynics reply that this same statement can be made of any field.)

Advanced Undergraduate Courses—Seminars

Typical undergraduate programs preparing students for graduate work in chemistry may require from 36 to 60 units, with about 45 as a mean. About 32 of these are usually allocated to the "four basic courses." Thus, all schools require more than these four, but the variation is a factor of about 8 in the number of advanced units expected. Actual variation is somewhat less than this, perhaps a factor of four, since most schools advise their students to take more than the minimum major if they are going to do graduate work. There does not, however, seem to be any real correlation between the amount of this advanced undergraduate work and performance in graduate school.

The important factors seem to be that the student have a choice of advanced courses from which he picks those he wishes to take, that the whole staff of the institution be familiar with all the basic and advanced courses and adapt their own advanced courses appropriately, that there be no sharp divisional lines within the chemistry department, that the course load be distributed through the full four years (but many taper off in the senior year), that no attempt be made to cover all possible fields in chemistry but that intensive coverage of certain areas be undertaken (some students will have trouble with certain ideas in graduate school, others with different ones depending on past training, but a good undergraduate education will insure that they will not draw blanks more often than they can fill them on their own).

Seminars designed for the undergraduates in which they report on their own research projects and on problems from the literature are an important adjunct of many successful programs. These are often required but given "no credit, just tea." Recording the talks and going over them with the student has merit. Assisting in the undergraduate laboratories seems most helpful to many students, with students from all three of the upper classes participating in some schools.

Undergraduate Research Programs

There is a widespread feeling among students and faculties that an introduction to actual research is one of the most helpful items for many undergraduates. This approach can be amplified by running many of the regular laboratories with a research approach, but a senior thesis with a written and an oral report is required in some schools and is optional in many.

It is in his research project that the student has the maximum opportunity to do library searches, select and follow individual problems of interest to himself, learn to meet distant deadlines, prepare written and oral presentations, and work out relationships between his abilities, which let him go it alone, and his deficiencies, which lead him to consult with his supervisor. It is most important that he not be merely "a pair of hands" for his supervisor.

Some schools have resolved the conflict between the pressure for more course work and for student research by concentrating almost all their research in the summer. Funds can usually be found to hire the students and to purchase equipment for either summer or academic year work so that the prime limitation now seems to be student and faculty interest and ability.

Summer work is not limited to that between the junior and senior years; all four summers may be used and some schools are inviting pre-college, high school graduates, regardless of what college they eventually plan to attend, to participate in the local programs. Few schools give both credit and financial recompense for research work, and most summer work is done for pay.

Publication is not normally held out as an end to the research, but a very respectable number of undergraduate research problems do yield solutions which appear in the professional journals.

New Areas for the Undergraduate Curriculum

The rapid growth of scientific knowledge is well-recognized, and the pressure to include the newest developments in our constant volume curricula is continual. It is essential that some of the newest developments be included so that each student is occasionally brought close to the actual frontier of the subject, so that he sees where the growth is occurring and becomes acquainted with the existence of both satisfactory and false interpretations of contemporary developments. If these frontiers are those being investigated in his own school, so much the better, but, as long as the student realizes the problem of encompassing contemporary ideas, it is not desirable to try to cover all of these ideas in the curriculum. He will be prepared for them when he meets them and will meet them on a reasonably wide front as he gets acquainted with the original literature.

Some ideas are so important, and so widely missing from current curricula, that their inclusion ought to be considered. These were listed: intelligent safety practices in every chemical laboratory (which are now missing in practically all of them), chemistry at high temperatures, surface chemistry beyond the usual passing introduction to colloid chemistry, solid state chemistry at a level beyond the general course but not involving the full contemporary treatment, magnetic effects including susceptibilities, more assigned or strongly suggested summer reading, and biochemistry with the accent on the chemistry.

Foreign Languages

Most graduate schools currently require a reading knowledge of German and either French or Russian. The German preference is based largely on the existence of many standard compendia in the language as well as on the vast amount of early literature which will probably never be translated, yet must be used. Some feel that an intensive knowledge, including conversational ability, in one language will supersede the present requirement before too long. Present general experience is that a student starting graduate school without the ability to pass the language exams quickly has a hurdle of real dimensions before him.

Non-Science Courses

Typical curricula preparing students for graduate work in chemistry divide into one-third of the work in the major field, one-third in related scientific fields, and one-third in non-scientific areas. This last requirement confers so many benefits on the typical student both in his professional and non-professional life that it should not be sacrificed to the continual pressure in the other areas. Several colleges and graduate schools are currently considering accelerated programs leading to the Ph.D. degree in a total of about six years, perhaps eliminating the Bachelor's degree and certainly eliminating the Master's degree entirely. Regardless of the length of the total program (and flexibility should be encouraged here as in all educational programs), shortening would be unwise in the non-scientific areas. It is much better to accelerate by diminishing scientific overlap and by relying on the high scientific ability of the talented person to discover and fill his formal gaps in science on his own.

Selection of a Graduate School

Almost any reasonably good student can now gain admittance to some graduate school. Most of the students who leave the more demanding schools by request move elsewhere and obtain a Ph.D. The growth in openings identified as graduate school space has currently outstripped the supply of talent. This has, if anything, increased the merit of advising students thoroughly on graduate schools and helping them select ones where they will profit most. An outstanding aid to this is the Directory of Graduate Research published by the American Chemical Society. Every potential major should be urged to look it over. Once a student has been admitted to a graduate school he might well use the directory to aid in searching the literature for papers from that school so that he will be familiar with the general research areas available before he gets there. But it is even better if he uses this information in selecting the school originally.

Only rarely is it a wise choice to remain for an advanced degree at the student's undergraduate institution. It should be almost a matter of institutional policy to force him to go elsewhere for the Ph.D.

Most talented students will profit more in graduate schools having a minimum of formal requirements and a maximum in flexibility of programs, and in schools where they are strongly urged to participate in the teaching program but are given adequate supervision when they do so. Few people profit when the new graduate student has sole responsibility for running his "discussion group."

Graduate Record Examination

The Graduate Record Examination is now required by some schools and by some foundations granting fellowships. Many faculty do not realize that they can examine copies of this test by having their dean get a copy from the Educational Testing Service for this purpose. Many of the questions concerning the examination could be better phrased if more people examined it.

Yet some of the best informed continue to raise two questions concerning the examination: (1) is it sufficiently flexible to be used fairly in schools with unconventional curricula (item—a recent examination had more of an emphasis on the Fresenius type of qualitative scheme than many schools deem reasonable), (2) should an examination which is intended to select those who are capable of graduate work also be used to select the top members of this group for fellowship awards? It would seem that reasonable answers to both questions might be available on the basis of experience to date.

It might be well to collect the placement examinations used by a cross section of the graduate schools and publish them annually. This would minimize the importance of local emphases and would keep the undergraduate institutions and the writers of national examinations closely informed on the type of education a representative section of the graduate schools feels is important. It would allow a steady change in emphasis as this seemed necessary and would record this change. The possible lag of a year or two inherent in this system would be much less serious than the currently possible lag of five to ten years or more. The Committee on Professional Training is taking this suggestion under advisement.

Conclusion

The conferees agree that this conference, as most, made no startling discoveries, that those in attendance profited more than any others, and that the few pages of summary cannot successfully capsulate the discussions or even include the informal contacts and exchanges. The value to those attending is difficult to assess, and the value to those who have a more indirect contact even more difficult to measure, but without such conferences and such indirect contacts, our educational system would surely loosen at the joints. For whatever advantages accrue to the interlocking of undergraduate and graduate work in chemistry as a result of this conference or to achieving the virtues listed earlier, the thanks of the profession go to the National Science Foundation for making it possible.

A science professor asked a student, "What is electricity?" The student puzzled, paused and finally resorted to the alibi, "I did know but I've forgotten." The professor smote his brow, "My God! The only man who ever knew what electricity is has forgotten!"

Philip J. Elving
and **Joseph M. Markowitz**
University of Michigan
Ann Arbor

Chemistry of Solutions in Liquid Sulfur Dioxide

As a solvent, liquid sulfur dioxide possesses interesting and potentially useful properties. It dissolves many inorganic compounds, has a much greater solubility for organic compounds than does water, and forms crystalline solvates with many solutes. Although its electrical conductivity in the pure state is low, its solutions are frequently good conductors. A variety of chemical reactions can be carried out in sulfur dioxide solution which have exact counterparts in other solvents; on the other hand, some reactions are peculiar to this solvent. Almost exclusively among useful solvents, liquid sulfur dioxide contains no hydrogen and no anions such as hydroxyl or halide. Its experimental manipulation, though more complicated than that of many other solvents, offers no formidable difficulties. Though toxic, the substance is not especially dangerous since it is irrespirable and even minute concentrations in the atmosphere are easily detected. Sulfur dioxide is relatively easy to purify; it can be purchased in an anhydrous grade and need only be passed through sulfuric acid to remove traces of SO_3 and through P_2O_5 to remove traces of water.

General Properties of Liquid Sulfur Dioxide

Table 1 lists values of properties of sulfur dioxide pertinent to its use as a solvent. Its melting to boiling point range makes liquid sulfur dioxide suitable for use as a solvent, while the low dielectric constant and the relatively larger molar volume indicate that its solvent properties will be much different from those of water. The conductivity of pure liquid sulfur dioxide is of the order of that of water; the conductivity of its solutions, though less than those of aqueous solutions, is still appreciable. Sulfur dioxide therefore falls into the class of what Jander (*1*) calls "water-like" solvents.

Table 1. Properties of Sulfur Dioxide

Property	Temp., °C	Value	Reference
Heat of vaporization	−10.0	5960 cal/mole	(*2*)
Heat of fusion	−75.5	1969.1 cal/mole	(*2*)
Dielectric constant	−16.5	17.27	(*59*)
	−68.8	24.63	(*59*)
Specific conductivity	−65.0 to −20.0	$3–5 \times 10^{-7}$ ohms^{-1}	(*5*)
	−17.0 to 0.0	$1–3 \times 10^{-7}$ ohms^{-1}	(*6,7*)
Molal ebullioscopic constant	...	1.45 deg/mole	(*1*)
Viscosity	0.0	0.0039 poise	(*1,60*)
	−10.0	0.0043 poise	(*60*)
Specific gravity	−10.0	1.46	(*3*)
Boiling point	...	263.08°K	(*2*)
Freezing point	...	197.64° K	(*2*)
S-O distance	...	1.46 ± 0.02 A	(*61*)
O-S-O angle	...	122 ± 5 deg	(*61*)
		129 ± 4 deg	(*2*)
Vapor pressure[a]	0.0	1163 mm	(*3*)
	20.0	3.23 atm	(*3*)

[a] Giauque and Stephenson (*2*) present the following equation for the vapor pressure of liquid sulfur dioxide from 197.64° to 263.5°K:

$$\log P = -(1867.52/T) - 0.015865T + 0.000015574\,T^2 + 12.07540$$

Because of certain discrepancies in the literature, two of the constants presented in Table 1 require comment. The freezing point of −75.5°C, taken from the calorimetric work of Giauque and Stephenson (*2*), is certainly more nearly correct than the earlier value of Cady and Taft (*3*). This is important, inasmuch as an otherwise excellent and authoritative monograph (*4*) presents the earlier value (−72.7°C) with the recommendation that it be used as a criterion of purity. There is also variation in the reported values of the specific conductance of pure sulfur dioxide, which has been ascribed by Cruse (*5*) to the use of inferior conductometric equipment by early investigators and partly to traces of water in the sulfur dioxide samples studied. Cruse's data compare well with those of Lichtin, Bartlett, and Glazer (*6, 7*); adequate precautions appear to have been taken in both cases.

Solvent Properties of Liquid Sulfur Dioxide

Solubility. Inorganic substances are relatively insoluble in sulfur dioxide (*cf.* Table 2, adapted from a similar one given by Jander (*1*)). Certain regularities are evident in Table 2, the most striking being the variation among the alkali halogenides. Compounds such as aluminum chloride, which are ordinarily considered covalent, are considerably more soluble than salts having a typical ionic lattice. In fact, such substances as bromine, boron trichloride, carbon disulfide, iodine monochloride, and the various thionyl compounds are completely miscible with liquid sulfur dioxide (*4*). The group IV tetrahalogenides and liquid sulfur dioxide

Table 2. Solubilities of Some Inorganic Compounds in Liquid Sulfur Dioxide at 0°C[a]
(Millimoles per 1000 g of SO_2)

Ion	F^-	Cl^-	Br^-	I^-	SCN^-	SO_3^{--}	SO_4^{--}
Li^+	23.0	2.8	6.0	1490.0	...	...	1.5
Na^+	6.9	ins.	1.4	1000.0	80.5	1.4	ins.
K^+	3.1	5.5	40.0	2490.0	502.0	1.6	ins.
Rb^+	...	27.2	...	...	...	1.3	...
NH_4^+	...	1.7	6.0	580.0	6160.0	2.7	5.1
Tl^+	ins.	0.3	0.6	1.8	0.9	5.0	0.4
Ag^+	ins.	0.1	0.2	0.7	0.9	ins.	ins.
Mg^{+2}	...	1.5	1.3	0.5	...	...	...
Hg^{+2}	...	3.8	2.1	0.3	0.6	...	0.3
Pb^{+2}	...	0.7	0.3	0.2	0.4	...	ins.
Al^{+3}	...	v.s.	0.6	5.6	...	...	...
Sb^{+3}	...	575.0	21.8	0.3	...	...	...

[a] Adapted from reference (*1*).

are miscible in all proportions above some critical temperature which varies from compound to compound (*8*).

Organic compounds are generally quite soluble in sulfur dioxide, the most notable exception being the saturated aliphatic hydrocarbons; this selective solubility in liquid sulfur dioxide is frequently utilized for separating aromatic from aliphatic hydrocarbons during the processing of crude oils. Iodoform is sparingly soluble; halogenated and nitrated aromatic compounds are very soluble. Alcohols, phenols, acids, and esters are all soluble, as are the basic compounds. In most cases, complete miscibility is possible.

Water dissolves in sulfur dioxide, but the extent of its solubility has never been very accurately determined. Wickert (*9*) reported the existence of a compound, $SO_2 \cdot H_2O$, which remains as a stable residue upon the evaporation of sulfur dioxide from the solution of water in sulfur dioxide at 0°C. He also reported that the equilibrium solubility of water in liquid sulfur dioxide at +22°C is 2.3 ± 0.1 g per 100 g of solvent. Conductivity measurements indicate some degree of solubility at temperatures lower than 0°C (*1, 9*). Dissolved water strongly affects solubility of other substances, as well as the electrical properties of their solutions; the direction of the change apparently varies with different materials (*1*).

Highly colored solutions frequently result when fairly soluble substances are dissolved in liquid sulfur dioxide; exceptions are the alkyl ammonium chlorides and bromides, aromatic hydrocarbons, alcohols, acids and esters derived from saturated hydrocarbons, and bases such as acetanilide. Most commonly, the solutions have a yellow color, regardless of the color or lack of color of the pure solute, indicating some similarity in the nature of the solvation phenomenon which occurs. Frequently, highly colored solutes exhibit a different color upon dissolution, e.g., iodine solutions are wine-red (*1*).

Useful sources for detailed quantitative solubility data include the monographs by Walden (*10*) and by Jander (*1*) and references (*8, 11, 12, 13*).

Solvate Formation. Sulfur dioxide forms stable solvates with many substances, analogous to the crystalline hydrates formed with water. These solvates have been studied in detail and the regularities encountered in the relationship between ionic size and the tendency to form solvates have been discussed (*1, 14*). The molar ratio of sulfur dioxide to adduct in the solvate is generally one of small whole numbers, but ratios as large as 14 have been reported (*14*). Generally, for inorganic salts the ability to form solvates parallels the solubility. Typical classes of compounds which form stable solvates include the alkali and alkaline earth metal iodides and thiocyanates, the alkali metal salts of fatty acids, tetraalkylammonium salts, and triarylmethyl halogenides. The solvates have a definite decomposition temperature at atmospheric pressure; many of them are stable to temperatures as high as 80°C. The heats of solvation are generally smaller than those of the ammoniates and hydrates of the same solutes.

Electrical Conductivity. The ability of sulfur dioxide solutions to conduct electric current is well known and has been extensively investigated (*1, 10, 12, 15*). The Ostwald dilution law is followed by strong electrolytes, but only at extraordinary dilutions (*1*); at such dilutions, the law of independent mobility of ions is also followed. Jander and Mesech (*15*) give the following order of ion mobility:

$$SCN^- < Br^- < I^-;\ N(CH_3)_4^+ < K^+ < NH_4^+ < Rb^+$$

On the other hand, the order of increasing conductivity—and, therefore, dissociation—parallels the order of increasing cationic size:

$$Na^+ < NH_4^+ < K^+ < Rb^+ < (CH_3)_4N^+ < (C_6H_5)_3C^+$$

For anions, the following order, which is not that of anionic size, exists:

$$SCN^- < ClO_4^- < Cl^- < Br^- < SbCl_6^-$$

The magnitudes of the equivalent conductances of sulfur dioxide solutions of typical strong electrolytes approach those of the same electrolytes in aqueous solutions, e.g., at a dilution of 1000 liter/mole, the equivalent conductance of potassium iodide is 147.9 $ohms^{-1}$ in water at 25°C and 118.8 $ohms^{-1}$ in sulfur dioxide at −10°C. Conductivities of this order of magnitude are exhibited by alkali metal, ammonium and tetraalkylammonium halogenides, and thiocyanates, as well as by some rather unexpected substances such as bromine, iodine, phosphorus(III) bromide, acid chlorides, tertiary amines, triarylmethyls, and triarylmethyl-halogenides. On the other hand, trialkylammonium salts are poor conductors, as are most thionyl compounds, sulfites, and typical aquo acids, e.g., hydrogen chloride (*1, 4*). The equivalent conductances at a series of dilutions for potassium halogenides, tetramethylammonium bromide, and twelve alkyl and aryl derivatives of triphenylchloromethane have been measured by Lichtin and Leftin (*16, 17*) who were able to demonstrate that the triarylmethylhalogenides associate in solution covalently as well as electrostatically.

By extrapolating the equivalent conductance to infinite dilution and making the assumption that the conductance ratio is equal to the degree of dissociation, values of the dissociation constants of a number of compounds have been calculated at various dilutions (*15*). These are of the order of 10^{-3} at 0°C for strong electrolytes, e.g., KI and $(CH_3)_4NI$. Extrapolation was carried out by means of the Ostwald dilution law; the dissociation constants for dilutions greater than 8000 liter/mole are substantially constant. However, the dissociation constants reported by Lichtin and Leftin (*16, 17*) were determined by the use of the Shedlovsky procedure (*18*) and are probably more reliable; values for the potassium halogenides at −8.93°C vary from 1.08×10^{-4} for KCl to 4.3×10^{-4} for KI with the values being larger at lower temperatures; the dissociation constant for triphenylchloromethane is reported to be 1.3×10^{-4} at −17°C.

The van't Hoff *i* factor has been measured by the ebullioscopic method for a variety of solutes (*15*); the factor is defined in the reported work as the theoretical molecular weight divided by the observed molecular weight, based on the molal ebullioscopic constant of 1.45° per mole. For non-electrolytes, *i* was found to be approximately one; other solutes give values both greater and less than 1. Binary electrolytes are apparently more or less strongly associated in concen-

trated solutions, as indicated by i values less than 1; however, i increases with increasing dilution to values greater than 1 and presumably approaches 2 for infinite dilution. Tetramethylammonium salts are distinctly anomalous in that their i factors tend to increase rapidly at high concentrations. Extensive polymerization is encountered, for example, in KSCN, for which i becomes less than 0.5 in concentrated solutions.

Reactions in Liquid Sulfur Dioxide

Among the various types of reactions which have been reported to occur in liquid sulfur dioxide solution are the following illustrative examples discussed by Jander (*1*):

Solvate formation:

$$KI + 4SO_2 \rightarrow KI\cdot(SO_2)_4 \quad (1)$$

Solvolysis:

$$PCl_5 + SO_2 \rightarrow POCl_3 + SoCl_2 \quad (2)$$

Metathesis:

$$Cs_2SO_3 + SOCl_2 \rightarrow 2CsCl + 2SO_2 \quad (3)$$

$$2AgC_2H_3O_2 + SOCl_2 \rightarrow 2AgCl\ (s) + SO(C_2H_3O_2)_2 \quad (4)$$

$$KI + (CH_3)_3NHCl \rightarrow KCl\ (s) + (CH_3)_3\,NHI \quad (5)$$

Oxidation-reduction:

$$6KI + 3SbCl_5 \rightarrow 2K_3(SbCl_6)\ (s) + SbCl_3 + 3I_2 \quad (6)$$

Complex compound formation:

$$Co(SCN)_2\ (s) + 2H_2O \rightarrow Co(H_2O)_2(SCN)_2 \quad (7)$$

From the organic side, only two or three suggestive items need be cited. Liquid sulfur dioxide is an excellent medium for the reaction of acid chlorides with ketene; the yields, for example, are twice those found when using chloroform as solvent (*19*). Double bonds in steroids often migrate in liquid sulfur dioxide solution; this phenomenon is often advantageous for isomerizing steroids (*20*). Sulfur dioxide has been suggested as a protein solvent (*21*).

Theories of Chemical Reactivity in Liquid Sulfur Dioxide

The Walden Theory. Walden (*12*), in attempting to place the chemistry of liquid sulfur dioxide on a firm basis, sought to explain the observed small conductivity of pure sulfur dioxide as well as the reported cathodic deposit of sulfur on electrolysis, subsequently discussed, by a presumed auto-ionization of sulfur dioxide into positively charged sulfur ions and negatively charged oxygen ions:

$$SO_2 \rightleftharpoons S^{+4} + 2O^{--} \quad (8)$$

Steel (*22*) had earlier used this formulation in discussing his electrolysis results. Later investigations (*3*, *23*, *24*, *25*, *26*) of electrolysis products are not in agreement, however, about the nature of the cathode deposit; it appears that sulfur is deposited only upon application of high voltages and, possibly, in the presence of water as an impurity. Moreover, the existence in solution of uncombined sulfur in a IV oxidation state seems unlikely.

The Sulfite Concept. Jander and his collaborators are responsible for a great deal of the fundamental research on the chemistry of liquid sulfur dioxide solutions. In seeking to unify the results of these investigations and to avoid the difficulties of Walden's theory, Jander and Wickert (*27*), following a suggestion of Cady and Elsey (*28*), proposed the "sulfito" concept of reactions in liquid sulfur dioxide. This theory was extensively discussed by Jander and his co-workers (*9*, *14*, *15*, *27*) and is used as a unifying principle in Jander's monograph (*1*). Because of its wide acceptance and because its validity has been seriously challenged in recent years, the theory will be discussed in some detail.

In the sulfito theory, the following mechanism of auto-ionization for liquid sulfur dioxide is assumed:

$$SO_4 = SO^{++} + O^{--} \quad (9)$$

The anion is then solvated, so that the overall reaction is

$$2SO_2 \rightarrow SO^{++} + SO_3^{--} \quad (10)$$

The thionyl and sulfite ions are assumed to have real existence and functions analogous to those of the acidic and basic ions, respectively, formed during the auto-ionization of water:

$$2H_2O \rightarrow H_3O^+ + OH^- \quad (11)$$

If this analogy is to hold extensively, thionyl compounds must be considered acid-analogous and sulfites, base-analogues. The reaction between a thionyl compound and a sulfite to produce a salt and solvent would then be considered neutralization:

$$Cs_2SO_3 + SOCl_2 \rightarrow 2SO_2 + 2CsCl \quad (12)$$

Other types of reaction, such as metathesis, solvolysis, etc., which are characteristic of solvents like water, have already been mentioned. Many of them can be followed conductometrically, and the results have been used in support of the sulfito concept. In addition, reactions depicting amphoteric behavior in terms of thionyl acids and sulfite bases have been reported (*29*). The sulfito system, with its emphasis on ionic reactions, was used with great advantage in systematizing these results, as well as in clarifying conductivity and related phenomena (*1*).

Obviously, the sulfito concept is a variation of the acid-base theory of solvent systems, originally suggested by Franklin (*30*), and shares the weaknesses of all such solvent systems: undue emphasis on the solvent, ionization, and ionic reactions (*31*). In addition, there has been an accumulation of evidence in the recent literature which renders the validity of the sulfito concept doubtful in any but a mnemonic sense.

Schattenstein (*32*) and Cruse (*5*) pointed out that the sulfito system depends on the definition of the neutralization reaction as the central characteristic of acidic and basic functions. The theory is therefore too closely oriented with the solvent. Other aspects of experimental behavior, such as the ability to change the color of indicators and conductivity relationships, are also characteristic of acid-base properties (*31*, *33*, *34*). Thus, from the indicator standpoint, the change of color of aniline from yellow to colorless when trichloroacetic acid is added to its solution in sulfur dioxide can only be explained by the assumption that trichloroacetic acid is functioning as an acid in the Brønsted sense (*35*). The reverse color change when quinone is afterwards added can be explained only by the assumption that quinone is a stronger base than aniline. The reaction scheme proposed (*32*) is:

$$An + SO_2 \rightarrow An\cdot SO_2\ (\text{yellow}) \quad (13)$$

$$An\cdot SO_2 + HA \rightarrow AnH^+ + A^- + SO_2\ (\text{colorless}) \quad (14)$$

$$AnH^+ + Qu \rightarrow HQu^+ + An \quad (15)$$

$$An + SO_2 \rightarrow An{\cdot}SO_2 \text{ (yellow)} \quad (16)$$

Cruse (*5*) found that the potential of the hydrogen electrode in liquid sulfur dioxide is reproducible and affected in a predictable way by the addition of Brønsted acids and bases; sulfur dioxide, contrary to the views of Wickert (*9*) and Jander (*1*), must consequently possess appreciable proton affinity. Evidence of buffer action in terms of proton transfer has also been presented (*5*). The protolytic acids and bases show a relative proton affinity in sulfur dioxide of more or less the same order that they do in water; thus, hydrogen chloride is a strong acid and diethylamine is a strong base with respect to their effect on the potential of the hydrogen electrode. The earlier work of West and Arthur (*36*) has been interpreted to mean that dipole-dipole interactions with the solvent are too weak to cause dissociation of the HCl molecule; it must be concluded that the hydrogen electrode behavior results from an actual proton transfer. Cruse's work has thus shown that interpretations of sulfur dioxide chemistry alternative to that of Jander can be made, interpretations not only intrinsically reasonable, but having substantial experimental support.

There is much direct evidence which challenges the sulfito concept. For example, Bateman, Hughes, and Ingold (*37*) assert that Jander's sulfito system is based on two experimental results: (*a*) the occurrence of reactions in liquid sulfur dioxide in which chlorine is displaced from thionyl compounds as chloride ion by means of other anions including sulfite; and (*b*) a supposed proof that the structure of amine solvates involves a complexing of the amine by thionyl ion to form a cation, sulfite being the anion:

$$2R_3N + 2SO_2 \rightarrow [(R_3N)_2SO]^{++} + SO_3^{--} \quad (17)$$

The cation structure is then supposed to be preserved intact through metathetical reactions.

Since it is not necessarily true that the stoichiometry of a reaction is indicative of its mechanism, Bateman, Hughes, and Ingold rejected (*a*) as a proof for the sulfito theory. In considering (*b*), they found that Jander's work in establishing the amine solvate structure contains a calculational error which makes the structure untenable. On repeating the work, they found that the solvate structure is best represented by a simple solvation formula $R_3N{\cdot}SO_2$. This compound could obviously not be involved in any further metathetical reaction such as to leave an SO entity intact, as Jander claimed. However, the compound $Et_3N{\cdot}SO_2$ was found to absorb atmospheric moisture and oxygen to form (Et_3NH)-HSO_4. The latter has almost the same analysis as Jander's supposed solvate and similar physical properties. It was concluded that this coincidence is the source of Jander's error.

Other amine solvate studies tend to support the contention of Bateman, Hughes, and Ingold. Burg (*38*), by a careful tensiometric study of methylamine and amine oxides in liquid sulfur dioxide, concluded that there was clear evidence against the formation of a compound such as $[(R_3N)_2SO]^{++}SO_3^{=}$. Bright and Jasper (*39*) reached the same conclusion from parachor studies. Actually, Ulich (*40*) had given an interpretation of the structure of amine solvates similar to that of Bateman, Hughes, and Ingold, even before the researches of Jander and his co-workers were published.

Undoubtedly the weightiest evidence against the validity of the sulfito system is that of exchange reactions involving tagged oxygen and sulfur atoms in liquid sulfur dioxide. Norris (*41*) has recently discussed the experimental observations and their consequences in detail. With O^{18} as a tracer, rapid exchange occurs between sulfur trioxide and sulfur dioxide (*42*) whereas no exchange is found in the same system when using S^{35} (*43*). The reported conductivity of sulfur trioxide in liquid sulfur dioxide (*1*) must therefore be ascribed to some scheme involving the mobility of oxide ions or oxygen atoms only; Huston (*43*) suggested

$$SO_2 + SO_3 = SO^{++} + SO_4^{--} \quad (18)$$

Such schemes as

$$2SO_2 = SO^{++} + SO_3^{--} \quad (19)$$

$$SO_3^{--} + SO_3 = S_2O_6^{--} \quad (20)$$

must be incorrect because they would lead to exchange of sulfur.

No exchange occurs between thionyl chloride and sulfur dioxide using O^{18} (*44*), a result which complements the negligible exchange found in the same system when using S^{35} (*45*). On the other hand, a rapid exchange occurs between tetramethylammonium pyrosulfite and sulfur dioxide, based on S^{35} (*45*). It can be concluded that the amount of thionyl ion present in sulfur dioxide solutions is much too small to account for the speed of sulfito "neutralization" reactions between thionyl compounds and sulfites. A further consequence is the probability that the sulfite-solvent exchange proceeds directly by a transfer of oxide ion between solvent and sulfite, rather than indirectly through the sulfito ionization:

$$SO_3^{--} + S^*O_2 = SO_2 + S^*O_3^{--} \quad (21)$$

Huston (*46*) has recently shown that such oxide transfer can occur rapidly even in the pure solvent in the form of condensed material on glass surfaces in equilibrium with vapor phase.

Since the assumed acid-analogue ions in any proposed acid-base scheme ought, at the very least, to be present in reasonable quantity under the prescribed experimental circumstances, it appears that the evidence reviewed effectively disposes of the sulfito concept.

Other Theories of Sulfur Dioxide Chemistry. Wickert (*47*) proposed an acid-base theory designed not so much to improve the sulfito theory as to extend the general solvent theory of acids and bases so as to make it independent of the solvent. To this end, "water-like" solvents are defined as substances which ionize to yield ions, of which only the negative ion has a closed electronic configuration. The definition of an acid is identical to that of the solvent. Salts and bases are defined as substances which ionize to yield ions, both of which have closed electronic configurations. This theory has been strongly criticized (*5*, *31*, *48*) on the ground that it ignores amphoteric properties. In addition, it contains many inconsistencies; e.g., Wickert is forced to regard hydrogen ion as having an open or incomplete electronic configuration although that of sodium ion is to be considered closed.

Other theories which have been applied to rationalize chemistry in liquid sulfur dioxide must be considered as fragmentary; they are not intended as complete theories, in the sense of the sulfito system, but are intended only to apply to certain aspects of liquid sulfur dioxide chemistry. Each is supported by specific evidence, but no claim has been made for their general applicability. Cruse (*5*) and Schattenstein (*32*), as indicated previously, have shown that the Brønsted protolytic theory of acid-base behavior (*35*) can be fruitfully applied in discussing electrode behavior and indicator color changes. Bateman, Hughes, and Ingold (*37*) suggest that the color of amine solvates as well as their electrolytic properties can be best explained by the hypothesis of electron transfer to form weakly dissociating radical ions, e.g., R_3N^+ and SO_2^-. Such compounds have been studied and extensively reviewed by Weiss (*49*).

Sulfito "neutralizations," if they occur at all, probably involve several steps, according to Bateman, Hughes, and Ingold, who predicted that the intermediate would be the ion SOX^+, rather than SO^{++}. This view has been confirmed by the work of Norris and associates (*42*, *50*, *51*) who studied radiosulfur exchange among thionyl halides, sulfuryl halides, and tetraalkylamine halides in both the pure state and sulfur dioxide solution. The exchange rates and equilibria are fully consistent with the existence of SOX^+ as an intermediate but not with that of SO^{++}.

It appears reasonable to assume that a comprehensive theory of chemistry in liquid sulfur dioxide may someday result from a synthesis of the various points of view outlined in the previous two paragraphs. The test of such a theory would be its ability to predict experimental behavior in unexplored areas. One such area is that of catalysis in liquid sulfur dioxide; this phenomenon is frequently used as an operational criterion of the acidic or basic character of the catalyst (*33*, *34*, *35*). Norris (*41*) has discussed acid-base catalysis of thionyl halide-sulfur dioxide radio-sulfur exchange and has shown the usefulness of the generalized acid-base concept of Lewis in systematizing the observed behavior. Cruse (*5*) has shown that potentiometric studies are feasible; accordingly, orientative studies with the many voltammetric techniques developed in recent years could be made. The success of any theory could be measured by its ability to allow quantitative interpretations of the results of such electrochemical studies.

Electrochemical Processes in Liquid Sulfur Dioxide

Conductometric measurements in sulfur dioxide solutions have been previously discussed in connection with the topics of electrical conductivity and of the interpretation of reactions on the basis of the sulfito concept.

A series of investigations on the use of liquid sulfur dioxide solutions for voltammetric and polarographic measurements has been in progress by the present authors and their associates for the past decade (*52*).

Electrolyses. Steele (*22*), who was the first to investigate the products of electrolysis in liquid sulfur dioxide solutions, reported that in the electrolysis of potassium iodide between platinum and other metallic electrodes, the current falls quickly from an initially high value to a much lower one and sulfur is deposited on the cathode. Later, Bagster and Steele (*53*) repeated and extended this work; upon the electrolysis of such salts as potassium, tetramethylammonium, and trimethylsulfonium iodides, both free sulfur and sulfite salts are found at the cathode; changes at the anode are similar to those in aqueous solution, e.g., free iodine is liberated. Anodes of active metals such as iron and zinc pass into solution as halogenide salts.

Centnerszwer and Drucker (*25*) found unstable products at the cathode when sodium or potassium iodide is electrolyzed. Careful analysis showed that the ultimately separated materials were thiosulfites and pyrosulfites; no sulfur was observed. It may be noted that thiosulfites and pyrosulfites are strongly reducing. On the other hand, at very high potentials achieved by the use of an unsymmetrical alternating current, electrolysis of pure, carefully dried sulfur dioxide produced a cathodic deposit of sulfur. This fact tends to invalidate some experimental conclusions of Wickert (*9*) in support of the sulfito theory. Wickert explained the increased conductivity of liquid sulfur dioxide containing dissolved water by assuming the formation of thionyl hydroxide, $(SO^{++})(OH^-)_2$, the ions of which he supposed to be more mobile than those produced by the ordinary sulfito ionization. He cited in support of this hypothesis the fact that on electrolysis of a water-sulfur dioxide solution at very high potentials, sulfur was deposited at the cathode and a gas (no analysis reported) was produced at the anode. However, from the results of Centnerszwer and Drucker (*25*), these same products correspond to the complete decomposition of pure sulfur dioxide; thus, the presence of water in Wickert's work was irrelevant. The discharge of true solute ions such as those of thionyl hydroxide would not ordinarily be expected to require the application of very high potentials. Yet even at 220 v, Wickert observed no gas evolution or sulfur deposit. It appears, therefore, that the increased conductivity of moist sulfur dioxide is not the result of a sulfito type ionization. In the light of Cruse's work (*5*), discussed earlier, it seems more reasonable to invoke the proton affinity of sulfur dioxide to explain the enhanced conductivity in the presence of water.

Cady and Taft (*3*), electrolyzed sulfur dioxide solutions of potassium iodide, thiocyanate, iodate, chlorate, and ferricyanate, and of ferric chlorate between various combinations of metal and metal-insoluble salt electrodes. In the cases of potassium salts, the cathode products were compounds of potassium with derivatives of the solvent, such as thiosulfites, sulfites, salts of thionic acids, and pyrosulfites. No deposit of sulfur was observed. The anode products were similar to those found in water.

However, the electrolysis products at the cathode do not always correspond to derivatives of the solvent. On electrolyzing triphenylbromomethane in liquid sulfur dioxide, the cathode deposit is triphenylmethyl (definitely identified by means of its peroxide derivative) and the anodic product is a mixture of triphenylbromomethane and its perbromide (identification not positive) (*26*). It is well known (*54*, *55*) that triphenylchloromethane dissociates into triphenylmethyl cation and chloride ion in liquid sulfur dioxide solution.

Anderson (*54*) has shown from the similarity of the absorption spectra of triphenylbromomethane and triphenylmethyl that the latter exists in sulfur dioxide solution in equilibrium with triphenylmethyl cation and an electron; the mutual compatibility of radical and cation makes the findings reported (*26*) seem quite reasonable.

On electrolysis of the free halogens and interhalogenides in liquid sulfur dioxide, using a silver cathode and a silver/silver bromide anode, the silver salts of the halogens were deposited at the anode and silver at the cathode, as would be expected in a similar aqueous electrolysis (*24*).

Bagster and Cooling (*23*), in what is now considered to be a classical proof of the existence of hydronium ions (*55*), electrolyzed solutions of hydrogen bromide and water in liquid sulfur dioxide. They found that water and hydrogen bromide dissolve in sulfur dioxide in equimolar proportions, indicating some type of compound formation; excess water formed a second phase. Upon electrolysis of the sulfur dioxide phase, the cathode products were water and hydrogen, and the anode product was bromine. Two possible types of compound can be formed between HBr and H_2O: a simple addition compound, $(HBr)\cdot(H_2O)$, and an oxonium compound with proton transfer, H_3OBr. In the former case, electrolysis would precipitate water at both electrodes with the faradaic amounts of hydrogen and bromine being produced at the cathode and anode, respectively. Since water was produced only at the cathode, the oxonium formulation, involving what is now called the hydronium ion, was considered to be correct.

Electrode Potentials. Electrode potentials in liquid sulfur dioxide were studied very little before the work of Cruse (*5*). Bagster and Steele (*56*) found reproducible potentials for cells such as $Zn\,|\,ZnBr_2$ (sat.), $SO_2\,|\,HgCl\,|\,Hg$; the potentials were affected by the addition of common ion salts in the same way as those of the corresponding aqueous cells. Potentials were measured with a quadrant electrometer, since it was found that the electrodes possessed such an extremely low capacity, that potentiometric currents were sufficient to cause polarization. Potentials for the three metals, zinc, cadmium, and lead, in saturated solutions of their salts versus mercurous chloride/mercury were reported. Cruse (*5*) later observed a similar result for the $Pb/PbCl_2$ electrode versus calomel, but found that the potential changed considerably more with time than Bagster and Steele had reported. Wickert (*57*, *58*) reported the potential of the hydrogen electrode versus mercurous chloride/mercury to be 0.3 v in a solution of hydrogen chloride (concentration not specified) in liquid sulfur dioxide, and the potential of the oxygen electrode (presumably versus the same reference electrode, though this is not stated; the nature and concentration of the solution are also not specified) to be 0.2 v. These values are of the same order of magnitude as those reported by Cruse (*5*).

The electrode potential measurements of Cruse (*5*) are the most extended, detailed, and careful yet made in sulfur dioxide. In view of the controversy surrounding the concept of the sulfito system, it is surprising that his paper, with its application of the Brønsted theory to sulfur dioxide, as discussed earlier, has not received any attention. According to Cruse's results, the silver/silver chloride and silver/silver bromide electrodes are stable in liquid sulfur dioxide solutions of their salts, though the latter electrode does not maintain as constant a potential over long periods of time as the former. The mercury/mercurous halogenide electrode undergoes considerable change of potential over a short period of time and is suitable as a reference only for measurements of short duration. These potential changes are not well understood; Cruse suggests a "solvation" of the electrode about which he is not very clear. It appears that either the "solvation" process itself or the gradual decrease of "solvation" with time is then responsible for the shifts. Cruse found the hydrogen electrode to be very reliable and the best of all the reference electrodes studied.

In studying the effects of changes in concentration of the electrolyte salt and of the addition of acids and bases, Cruse found the behavior of a cell in liquid sulfur dioxide to be generally similar to that of the same cell in water, e.g., the silver/silver chloride electrode shows the correct potential change per unit concentration change versus the hydrogen electrode. On the other hand, the potentials measured do not agree very well with those calculated from thermal data. For example, the measured value of the potential for the cell

$$Ag\,|\,AgBr\,|\,0.03\ M\ KBr,\ SO_2\,|\,H_2\,|\,Pt$$

is -0.461 v, while the calculated value is -0.166 v. Since no active depolarizer was present and no hydrogen sulfide was given off (from a possible reaction of hydrogen with sulfur dioxide), Cruse believed that the difference can be accounted for only by some form of "solvation" of the silver/silver bromide electrode. Exactly the same situation exists for the silver/silver chloride electrode.

Cruse found a potential for the oxygen electrode versus the silver/silver bromide electrode so far different from the calculated value that the oxygen electrode must be considered irreversible.

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James C. Sternberg[1]
Michigan State University
East Lansing

Rapid Preparation of Lantern Slides

It is frequently difficult or impossible to plan lantern slides sufficiently in advance of their use to have photographic slides prepared. Lantern slides prepared by typing on paper or by use of various commercially available slide materials frequently lack the desirable sharpness of definition.

A new method which has been found to give highly satisfactory slides is the direct transfer of the surface of a "Ditto"* carbon sheet to a glass slide. The content of the slide is first laid out on a sheet of tracing paper in just the way it is to appear on the slide. A lantern slide cover glass is then placed in proper position under the tracing paper, and a "Ditto" carbon sheet (or a piece cut from one) is inserted between the tracing and the glass, with the waxy transfer surface toward the glass. The proper juxtaposition can be stabilized by judicious use of masking tape. The content of the slide is then traced directly on the tracing paper, using a ball point pen or a sharp (medium to hard) pencil, transferring the information from the "Ditto" carbon to the glass; only a little practice is required to find the optimum pressure. Errors can be corrected by erasure from the slide with a razor blade. To insert the correction, a small fresh piece of "Ditto" carbon must be inserted in the proper place.

The slide can be used directly as a single piece of glass, or it may be protected against smearing by covering the printed side with a clear slide cover glass and binding the pair as a normal slide. The waxy lettering gives sharp, clear images upon projection and shows no tendency to wilt upon prolonged exposure to the heat and light of the projector.

The glass can be cleaned with aqueous detergent or with organic solvents so that the glass can be re-used when the slide is no longer needed.

* "Ditto" carbon sheets are supplied by "Ditto," Inc., for use in preparing master sheets for fluid duplicator machines. Best results have been obtained through use of red carbons.

[1] Present address: Beckman Instruments, Fullerton, California.

Emanuel Kaplan
The Baltimore City
Health Department
Baltimore, Maryland

Chemicals in Food: Health Significance and Control

During and shortly after World War II, a tremendous increase occurred in the use of chemicals in the broad field of food technology. Regulatory officials viewed the situation with suspicion.[1] All chemical treatment of food was looked upon with distrust. The very words "chemical," "artificial," "synthetic" carried a stigma. In 1949, legislators from farm states became aware of the role of synthetic chemical emulsifiers in permitting bakers and other food manufacturers to cut down on the quantity of shortening and eggs in their products, and an outcry arose on the role of "ersatz" foods and their effect on the farm economy. From then on public reaction grew louder, and the allegations of reduced nutritional quality and the use of substances deleterious to health aroused the attention of medical, public health, scientific, and lay groups and stimulated the appointment in Congress in 1950 of the Delaney Committee, a House of Representatives Select Committee to Investigate the Use of Chemicals in Food Products.

Over a two-year period and in thousands of pages of testimony, the Delaney Committee inquired into the adequacy of present laws to protect the public welfare. These hearings emphasized that hardly a food is consumed which has not had some chemical treatment in its production, processing, packaging, or storage. One of the most effective disclosures was that of the Food and Drug Administration that of more than 700 chemicals employed in foods, only 428 were definitely known to be safe. The safety of the remainder had not been adequately established, largely because of lack of information as to chronic effects on humans; that is, the effect of regularly eating a quantity of this or that chemical over a period of years. This widely publicized committee statement caused apprehension as to the safety of processed foods. Some consumers made efforts to obtain foods grown without chemical fertilizer, fruits grown without insecticides, or bread made from unbleached flour. Though such food practices were without scientific justification, a public health problem did exist. Legislation to correct the situation was needed since existing Federal laws did not provide sufficient protection to the public. The 1938 Federal Food, Drug, and Cosmetic Act controlled the addition of outright poisonous substances, but left it up to the government to discover their use. Authorities had to prove them poisonous or deleterious, and court action was required to remove them from the market. The law was not preventive but merely punitive. Actually, what was needed was new legislation to require adequate advance or pretesting of chemicals termed "food additives" intended to be added to food and their approval before they are used.

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Chemicals Helpful and Necessary

By 1953, it was apparent from the literature that attitudes had changed.[2] Before condemning the presence of chemicals in food there were basic economic considerations. An increase in food production was needed to keep pace with a fast-growing population. Boosting the yield per acre of available land could only result from advances in scientific agriculture, prevention of agricultural waste, and improved methods of food manufacture, preservation, and storage. Destructive insects alone caused losses in excess of four billion dollars per year. Many crops could not be grown commercially without the use of insecticides. Losses due to weeds exceeded those caused by insects and plant diseases. Several hundred million dollars' worth of pesticides were used in the battle against insects, rodents, and plant diseases. The modern food industry in this country is a 70 billion dollar industry. More than 25% of the family income is spent on food. This industry could not operate without chemicals. Chemical applications were involved from the growing of food to its final packaging.

There is now a widespread use by the farmer of hundreds of organic chemical compounds tailor-made for such specific agricultural applications as soil conditioners, seed-treating compounds, fertilizers, insecticides, weed control agents, fungicides, rodenticides, soil fumigants, regulators of growth and maturation, preharvest defoliants or chemical frosts, antibiotics for plant disease control, and many others. In the past 25 years the total poundage of agricultural chemicals, exclusive of fertilizer, rose from 100 million to almost 2 billion pounds.

Food manufacture and preparation itself is now largely a matter of factory production controlled by chemical compounds designed for many purposes. Chemical research has provided a whole host of so-called "food improvers." There are retainers, modifiers, or inhibitors of virtually every property natural food may exhibit. Among these are new preservatives, mold inhibitors, anti-sprouting agents, fumigants, germicides, anti-oxidants, emulsifiers and stabilizers, shortening extenders, humectants, anti-staling agents, artificial flavors, flavor enhancers, tenderizers, artificial colors, firming agents, plasticizers, ion-exchange agents, vitamin and mineral enrichment chemicals, leavening agents, bleaching agents, acidifying ingredients, neutralizers, industrial enzymes, films and waxing compounds,

[2] KAPLAN, E., *ibid.*, **17**, 102–110 (1953).

artificial sweeteners, plastic wrappers, treated papers, fungicidal wrappers, lubricants, anti-foaming agents, propellants, baking pan glazes, and others. Also electronic, antibiotic, and ionizing radiation processing methods are being employed.

It is apparent that by the time food reaches the modern kitchen, chemicals have been intentionally added to serve some functional purpose in the control of manufacturing operations or in the modification of the food's physical properties, stability, or uniformity; or chemicals are incidentally or accidentally present as insecticidal residues or as contamination from packaging materials. There seems to be no limit to the growing list of chemicals that may find their way into the food supply. Since 1940, it is estimated that about 25,000 new chemical substances have been screened for possible use in food.

It is now generally conceded that chemical food additives have a very helpful and a very necessary place. One has only to visit a modern supermarket to see that the American public wants improved food products and convenience foods—the packaged biscuits and cake mix, instant coffee, precooked frozen foods, and many others. Whether to relieve starvation, to increase the variety of attractive foods, or to release women from the drudgery of the kitchen (and more than 20 million American women are gainfully employed outside their households), chemical food additives are here to stay but we must learn to use them safely.

The guiding principles of harmlessness and usefulness have not always motivated the food and agricultural chemicals industries in their desire to improve food products and methods of production and to make cheaper foods with greater customer appeal. In some instances, chemicals were actually used which later proved harmful.

Safety under Conditions of Use

Pesticides. Since World War II, there has been a great advance in insect control with the widespread use of synthetic organic pesticides. By and large, they are poisonous. More than 150 of them are now in use. The regulatory chemist is hard pressed to ascertain whether a food is contaminated and with what, and to estimate the degree of contamination. In some instances, there are no reliable quantitative methods of analyzing for certain insecticides and there are satisfactory methods for only a few. Some years ago, wide publicity was given to the fact that DDT used in spraying cow barns to control flies is absorbed and accumulates in the fat of animals and can be excreted into milk. Recent surveys continue to show that a significant percentage of market milk samples contain residues of pesticides.

Off flavors in fresh and processed foods such as potatoes, peanuts, and sweet potatoes, from the use of certain insecticides resulted in financial loss. In some instances, contamination of the soil left it unfit for production of certain crops. As a result of these instances and the use of other agricultural chemicals of a high order of toxicity on foods, in 1954 Congress passed the Miller Pesticide Chemicals Amendment to the Food and Drug Act. Under its terms raw agricultural commodities such as fresh fruits, vegetables, grain, milk, meat, and similar products cannot be marketed if they bear a residue of a pesticide chemical unless the chemical is generally recognized by experts as safe or the residue remaining on the food is within a safe tolerance limit set by the government. Because of the unique position of milk in the diet, no tolerance is permitted for pesticide residues in milk. Laboratory facilities are limited and quantitative tests for spray residues are difficult to make and are time-consuming. How can a packer of canned food protect himself to avoid seizure of his product after it is processed? He cannot wait for a laboratory report. The vegetables are perishable. He can protect himself only by buying his raw product from known growing areas where spray schedules are supervised to prevent excessive residues at harvest.

Hormones. In recent years it has become common practice for growers of poultry and livestock to employ synthetic hormones having the activity of female sex hormones to fatten, tenderize, and literally "chemically castrate" poultry and to increase the weight of livestock and to gain early marketing. Chickens treated by implantation of hormone pellets under the skin of the neck are sold as "caponettes." The Food and Drug Administration has seized poultry with hormone pellets still unabsorbed. At present, more than two-thirds of all beef animals in the United States are treated with hormones under a patent granted in 1954 to the Iowa State College Research Foundation and with the approval of the U.S. Food and Drug Administration. There has been some conflicting testimony as to the safety of eating the flesh of such animals but the preponderance of evidence indicates no hazard.

Antibiotics. There has been considerable research on the use of various antibiotics as food preservatives to reduce spoilage, to lengthen the keeping quality, and to modify the processing time of canned foods. In general, it is felt that antibiotics have no place in food as consumed. About ten per cent of the population has a tendency to react to penicillin. The use, or rather misuse, of antibiotics in the treatment of mastitis or udder infections in cattle has contaminated market milk supplies. Farmers are now directed to discard milk for three days following treatment. However, annual surveys for the past few years over the entire United States continue to show from three to eleven per cent of samples to contain penicillin. In 1957, the Food and Drug Administration knew of not one single case of proven reaction following ingestion of fluid milk known to contain penicillin. They consulted a panel of thirty medical authorities on the public health significance of penicillin in milk. The majority concurred in finding little likelihood of consumer harm but that a reaction might be caused in "exquisitely" sensitive persons and further studies were recommended with highly sensitive people. Very recently[3] a publication cited cases of chronic penicillin urticaria with cures using penicillinase, an enzyme which specifically inactivates penicillin, thus for the first time proving that penicillin-contaminated dairy products can cause allergic reactions.

Antibiotics are used in feeding of poultry and swine and stimulate growth, but this is not a public health problem since residues are absent in the meat. In 1955, the use of an antibiotic, chlortetracyclin, was permitted as a dip for uncooked poultry. This was the first permitted use of antibiotics on food. The birds are dipped

[3] ZIMMERMAN, M. C., *A.M.A. Archives of Dermatology*, **79**, 1–6 (1959).

for two hours in an ice water bath containing 10 ppm. Not more than 7 ppm of the antibiotic is left on the poultry. Since poultry is always cooked before it is eaten, there is no residue remaining on the cooked meat treated at this tolerance level. More than a half-billion pounds of fresh poultry have been treated in this manner. Recently permission for the use of this antibiotic was extended to aid commercial fishermen in keeping fresh-caught fish in a sound condition. As in the case of poultry, it is no substitute for sanitation and adequate refrigeration. It cannot make bad fish good, but it can make good fish remain satisfactory longer by retarding bacterial growth.

Flavorings. Chronic toxicity studies of a sweetening agent, dulcin, or *p*-phenetylurea, showed the substance to produce liver cancer when fed to rats at low dosage for two years; consequently, dulcin is now regarded as a poisonous material which has no place in food. The substance had been used for more than fifty years as a sugar substitute. Producers of coumarin voluntarily withdrew this flavoring agent from sale for all uses in food because pharmacologic research raised a question as to its safety. Coumarin had been used in synthetic flavors for 75 years.

Dyes. A re-examination is being made by the Food and Drug Administration of colors certified for use in food. Synthetic food colors are referred to as "coal tar colors." The term connotes a far cruder substance and is derived from the first synthesis in 1856 from chemicals occurring in coal tar. By 1906, more than 80 dyes were offered to the United States food industry. Colors known to be harmful were gradually eliminated. In 1908, seven colors were permitted for certification on a voluntary basis. In 1938, color certification became compulsory for coal tar colors that may be used in food, and the list grew to include eighteen colors which, according to the best scientific evidence then available, were harmless. The law required that an approved coal tar color must be "harmless" regardless of the amount used; harmless per se with no provision for a tolerance. During the past two years, using improved techniques and feeding the dyes to test animals at high dosage for long periods, some colors were found to produce adverse effects. As a result, two orange colors and a red color were removed from the list eligible for certification for food use, and proceedings were begun to ban four yellow colors used in coloring butter, oleomargarine, and other food items. There had been no report of harm to humans from the yellow colors, but the orange and red colors were related to instances of food poisoning involving highly colored popcorn and Halloween candy. The ban on the red color known as FD&C Red No. 32 was bitterly fought through the courts since it had been used to color the outer skin of Florida and Texas oranges for more than thirty years. Early oranges mature with skin still green and later oranges undergo a regreening of the rind. The orange-purchasing public requires an orange-colored rind and would not accept those with green rinds. A stay was granted until March, 1959. The Supreme Court upheld the Food and Drug Administration and Red 32 was banned on oranges effective March 1 of last year. In March of 1959, the Federal Act was amended to permit temporary listing and certification of a new dye, Citrus Red No. 2, for coloring mature oranges under tolerances found safe, pending congressional consideration of general legislation for the listing and certification of food colors under safe tolerances. This is based on the idea that the absolute harmless rule is impractical, and that safety should be related to the amount used.

In some European countries, scientists found carcinogenic or cancer-producing properties in some food colors. However, the dyes involved were not certified for use in food in the United States.

Two years ago at an international conference on cancer in Rome, reports were made that there are chemicals in use in food today which have not been studied sufficiently to make sure that they do not cause cancer in man. The word "cancer" has an alarming ring. Some say that a chemical should not be permitted in food if it produces any cancer in any experimental animal by any route of administration. Cancers can be produced in animals by repeated injections into muscle of sugar solution or of vegetable oils. Does this mean that sugar and vegetable oil should be eliminated as food? If a chemical is intended to be eaten in food, the fact that it could produce a tumor by injecting it under the skin should not rule out its food use. On the other hand, certain permitted food dyes on repeated injection under the skin produce tumors, therefore coal tar dyes are not permitted for coloring parenteral solutions (for injection).

Federal authorities state that there is no known cancer producer in our diet. But it is admitted that years of research will be required to build definitive knowledge concerning all causes of cancer. In the meantime, government agencies, the food industry, and the National Research Council are working together to facilitate the development of this knowledge. The National Research Council established a permanent committee on carcinogens. This is a twilight area and will take years to resolve. In the meantime, there is a public relations problem, a scientific problem, and a public health problem all rolled into one.

Radiation. The effect of the atomic age on the nation's food supply is of concern to regulatory officials and is receiving much attention in the press. There are two aspects to the problem. First, there is the possibility of radioactive isotopes getting into food. The sources could be waste products from applications of atomic energy such as nuclear power plants or fall-out from weapons tests, rendering radioactive the incoming raw materials and water supplies of food-processing plants. Recently a power reactor in England went out of control temporarily and pasture land was contaminated. As a result, all milk in a 200-square mile area was dumped. To establish safe radiation tolerances, to have a base line, hundreds of samples of canned foods packed prior to 1945 were gathered by government chemists to gauge radioactivity in modern foods as compared with those of the pre-atomic period.

The second problem is the safety of foods irradiated for preservation by electrons and gamma rays. This process of cold sterilization is being explored principally by the U.S. Army Quartermaster Corps to eliminate refrigeration in the handling of military supplies and to increase shelf life. Appraisal of the safety of the procedure is a complex problem. Radiation causes changes in some foods in color, odor, flavor, and texture. Foods so treated are regarded as containing chemical

additives. As yet the production of such food is on an experimental basis.

As a result of growing public concern since 1950 there has been a struggle between the Food and Drug Administration and consumers' groups on the one hand and those engaged in the production of food and food additives on the other. As the issues in this cold war clarified, there arose increased recognition of the difference between the terms "toxicity," which related to capacity to produce injury, and "hazard," which refers to condition of use. Today we speak of safety under condition of use, which means that any chemical additive, even a known poison, could be used in a harmless amount, provided it would serve some useful purpose or be of benefit to the consumer. Many food components, naturally present as well as added, are poisons in large amounts but are beneficial or even essential in small quantities. The addition of fluoride to drinking water to inhibit tooth decay is an example.

The Present Law

In September of 1958, the 85th Congress passed a Food Additives Amendment to the Federal Food, Drug, and Cosmetic Act. The law recognizes the need for additives in food but these chemicals must be pretested —tested in advance of use—to assure safety. The burden of proof is on the one proposing the new food additives and in most instances will require expensive and extensive testing by criteria for safety established by the Food Protection Committee of the National Research Council. A food chemical for use by man will not be granted a tolerance that will exceed $\frac{1}{100}$ of the maximum amount demonstrated to be without harm to experimental animals. A list of chemicals was provided which the authorities believed to be exempt from testing requirements of the law because they are generally recognized as safe for their intended uses. Commonly used substances such as salt, sugar, vinegar, are not listed. If a food additive is not listed or if it is not generally recognized by qualified experts as safe, then it cannot be used legally until permitted by regulation. The user of the chemical must petition for such a regulation and supply necessary scientific proof of safety.

Responsible food manufacturers realize that public acceptance is based on public confidence and most of them produce good, clean, wholesome food. We pride ourselves in the fact that our food is the safest and cleanest, most abundant and varied available anywhere. This is because of improvements in food production and technology in which chemicals have played an important role. However, consumers have a right to know what is going into their food. The new food additive law will do much to relieve fears about the safety of our food supply. Its passage brings to a close a major phase of a long legal battle to prevent the use in foods of chemical substances not adequately tested to insure their safety.

New Prefixes for Units

The National Bureau of Standards has decided to follow the recommendations of the International Committee on Weights and Measures to use new prefixes for denoting multiples and submultiples of units. The Committee adopted the prefixes at its meeting in Paris in the fall of 1958. In Addition to the 8 numerical prefixes in common use, which are given in the table below, the Committee expanded the list by adding the 4 prefixes marked with an asterisk. Thus, for example, 10^{-12} farad is called 1 picofarad, and is abbreviated 1 pf.

Multiples and Sub-multiples	Prefixes	Symbols
1 000 000 000 000 = 10^{12}	tera*	T
1 000 000 000 = 10^{9}	giga*	G
1 000 000 = 10^{6}	mega	M
1 000 = 10^{3}	kilo	k
100 = 10^{2}	hecto	h
10 = 10	deka	dk
0.1 = 10^{-1}	deci	d
0.01 = 10^{-2}	centi	c
0.001 = 10^{-3}	milli	m
0.000 001 = 10^{-6}	micro	μ
0.000 000 001 = 10^{-9}	nano*	n
0.000 000 000 001 = 10^{-12}	pico*	p

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D. B. Sowerby
and L. F. Audrieth[1]
University of Illinois
Urbana

Inorganic Polymerization Reactions

II. Addition polymerization

The first article of this series showed that condensation polymerization reactions can be employed to form higher molecular weight products by a number of different routes. Such processes include cationic and anionic aggregation reactions in aqueous solutions, in non-aqueous systems, and at higher temperatures in the absence of solvent. Condensation also occurs when hydrated, ammoniated, or solvated products undergo dehydration, deammonation, or desolvation at higher temperatures. Thermal elimination of other low molecular weight species frequently brings about condensation polymerization. Reactions of partial solvolysis, in which protonic solvents attack polyfunctional reactive inorganic compounds step by step, are often followed by condensation processes in which partially solvolyzed intermediates undergo polymerization by elimination of low molecular species. Interactions of polyfunctional organic molecules can conceivably be modified by replacing one of the reactants with a polyfunctional inorganic compound.

This second paper of the series will cover processes of addition polymerization in which such repeating units of the high molecular weight aggregates are identical with the monomers from which the polymers are derived. Other molecules or ions may participate in the polymerization process to serve as initiators or chain terminating end groups. Reactions of molecular association through hydrogen bonding and of processes in which elemental or molecular species undergo change to products of higher molecular weight are reviewed in this paper.

Hydrogen Bonding

The fact that a hydrogen atom can act as a bridge between two electronegative atoms has been recognized for many years. Hydrogen bonds result in the formation of aggregates in compounds such as hydrogen fluoride, water, and ammonia. Even though they are relatively weak (approximately 5 kcal) when compared with the energy of a normal covalent bond (approximately 100 kcal), they account for the anomalous properties of these substances in the liquid state. The melting points, boiling points, and heats of vaporization are all abnormally high when compared with the corresponding properties of the related hydrides in each of their respective groups in the periodic table. Hydrogen bonding also plays an important part in determining the physical properties of liquid hydrogen cyanide, hydrogen peroxide, and other polar hydrogen-containing and hydroxylic solvents. However, owing to the small energy involved, the hydrogen bond is readily broken and the degree of aggregation of a hydrogen bonded compound is rapidly reduced as the temperature is raised. Hydrogen bonding does not necessarily link together like atoms, but is operative in many systems in which the properties vary markedly from ideality. Hydrogen bonding phenomena also play a large part in such practical polymer applications as plasticizing action and the accompanying modifications of physical properties of such high polymers.

Allotropic Modifications of Elements as High Polymers

Sulfur

It is now considered from X-ray studies and theoretical calculations that the octatomic ring system (S_8) occurs in many of the modifications of sulfur. When liquid sulfur is heated, a distinct transition in physical properties begins to occur at 157°C. A thousandfold increase in viscosity is observed when the temperature is raised from 157°C to 187°C. The theory of Gee and co-workers (*70*, *71*), based mainly on an analysis of viscosity and heat capacity measurements, correlates the known facts concerning liquid sulfur. It is postulated that an equilibrium exists in liquid sulfur between S_8 rings and S_x (where x is variable) polymeric diradicals If iodine is added to liquid sulfur, the viscosity does not increase as rapidly, due almost certainly to the addition of iodine atoms to the ends of such sulfur chains, thus terminating the polymerization process. From the effect of iodine on the viscosity of liquid sulfur, Gee has calculated the maximum chain length to be in the order of 10^6 sulfur atoms; this figure is considered accurate to within an order of magnitude.

When homolytic cleavage of the ring systems occurs, giving rise to S_8 diradicals, unpaired electrons remain at the ends of such chains; liquid sulfur should thus be paramagnetic in behavior. Measurements on the magnetic susceptibility of liquid sulfur have been attempted, but the methods employed were not of sufficient sensitivity to detect any paramagnetism. The first direct evidence for the existence of radicals in sulfur has been obtained from a study of the more sensitive paramagnetic resonance absorption spectroscopy at temperatures between 189° and 414°C (*72*). One single res-

This is the second in a series of three papers on this topic to be published in THIS JOURNAL, based upon a paper presented before the Division of Polymer Chemistry at the 134th Meeting of the American Chemical Society, Chicago, September 1958. Literature citations and tables in this paper are numbered consecutively with those in the first paper.

For the first paper, see J. CHEM. EDUC., **37**, 2 (1960).

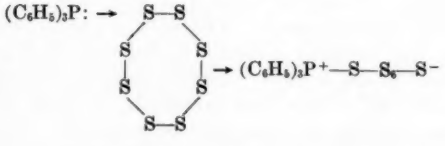
[1] At present, serving as Scientific Attaché at the American Embassy, Bonn, Germany.

onance line was observed at all temperatures; the intensity of absorption, however, increased with rising temperature. Thermal equilibrium was rapidly established in liquid sulfur and the intensity of the absorption depended only on the temperature of the sample and was not related in any way to the previous thermal history.

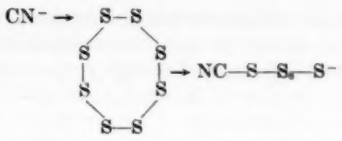
Analysis of the intensities and widths of the absorption line led Gardner and Fraenkel to estimate that the absolute concentration of unpaired electrons at 300°C is in the order of 10^{-3} moles l^{-1}. On the assumption that there are two independent unpaired electrons per sulfur chain, the concentration of chains is in the neighborhood of 6×10^{-4} moles l^{-1}. Further calculations have shown that the chain length reaches a maximum value of 1.5×10^{6} at 171°C. This estimate agrees quite well with the value calculated by Gee from the effect of iodine on the viscosity of molten sulfur.

The formation of the well-known plastic sulfur has long been used as evidence for the thermally initiated polymerization of sulfur. If liquid sulfur at a temperature above 160°C is cooled rapidly, an elastomeric product, capable of elongation to approximately eight times its original length, is obtained. X-ray diffraction patterns on the material under stress confirm the presence of long chain fibers. Plastic sulfur on standing reverts to a brittle mass consisting of the rhombic and monoclinic modifications, but the stability of the metastable phase can be enhanced by incorporating various substances such as the phosphorous sulfides into the plastic sulfur matrix.

It may be pertinent to mention here that the S_8 ring can be cleaved at room temperature, under such mild conditions that a homolytic splitting of the ring is obviated. In all reactions of this type it is considered that ring opening occurs by nucleophilic attack on a sulfur atom of the ring. A dipolar intermediate will result if attack is by a neutral nucleophilic agent. In the reaction between sulfur and triphenyl phosphine (*73*) giving triphenyl phosphine sulfide as the end product, the first step is postulated to be:



Subsequent rapid nucleophilic displacements with triphenyl phosphine will break the S_8 sulfur chains stepwise giving eight molecules of triphenyl phosphine sulfide. Kinetic measurements on this system in benzene solution are in agreement with a slow cleavage of the sulfur ring system (rate determining step), followed by rapid break-up of the sulfur chain. Addition of "ionizing solvents," e.g., water or methanol, causes an increase in the rate constant, which is in agreement with the postulation of a highly polar intermediate. The kinetics of the formation of thiocyanate from sulfur and cyanide (*74*) are also in agreement with a mechanism similar to that postulated above. The transition state in this case, however, is an anionic species and the rate of reaction is retarded by the addition of water to the methanol solvent.



For both reactions, however, strong irradiation of the reacting solutions appears to produce another form of sulfur which reacts at an immeasurably faster rate with the nucleophilic reagent, while the remaining sulfur reacts at the normal rate. In irradiated sulfur, the S_8 rings are already opened and the rate determining step in these circumstances is not the same as when the reaction is carried out in the dark.

Possibly, this concept of heterolytic cleavage of an S_8 molecule by a nucleophilic agent could be applied to reactions between sulfur and reagents such as the hydroxide and amide ions.

Phosphorus

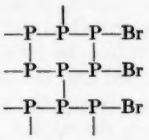
The P_4 tetrahedron is the basic unit in elementary phosphorus. It has been shown to exist in the vapor phase at temperatures up to 800°C and has been identified in fused white phosphorus by X-ray diffraction techniques. Three allotropic modifications of phosphorus have been prepared. These are (*a*) white phosphorus, which in the solid state consists of discrete molecules—most likely as P_4 tetrahedra—and is soluble in many organic solvents, (*b*) black phosphorus, prepared by heating the white modification at 200°C under high pressure—the crystal structure of this allotrope is similar to that of graphite, and (*c*) the so-called "violet phosphorus." This name covers a wide variety of different polymeric substances, varying markedly in color from orange-red to violet. The common red phosphorus and the modifications prepared by Schenck, Wolf, Pedler, etc., are included in this category. These various modifications are easily differentiated from the white allotrope by decreased chemical reactivity and insolubility in solvents such as carbon disulfide.

White phosphorus can be converted to the violet modification by the action of heat at 240–260°C; the reaction proceeds more rapidly in the presence of light. The color of the resulting product varies from red to violet and appears to depend on both the temperature and time of heating. The conversion of white to violet phosphorus can also be carried out in various solvents, and is significantly facilitated by the addition of substances such as bromine and iodine. This catalysis by halogens could entail either radical initiation or addition of positive halogen to phosphorus to bring about opening of P—P bonds.

All forms of red phosphorus have the ability to incorporate into the polymeric matrix the elements of the solvent in which the reaction was carried out. For example, Schenck's phosphorus, which is obtained by refluxing a solution of white phosphorus in phosphorus tribromide, contains up to 48% phosphorus tribromide. The bromide is held so tightly that it cannot be removed by extraction with solvents. Treatment with water results in the quantitative elimination of hydrogen bromide, together with formation of a new red phosphorus containing approximately 90% phosphorus and the elements of water.

Recent Russian work (*75, 76*) has shed some light on

the production of the various red modifications. It is believed that all red phosphorus products are polymers of the white allotrope and always contain definite end groups. In the case of Schenck's phosphorus, the end groups are bromine atoms; in common red phosphorus it is conceivable that the elements of water have been incorporated. Kraft and Parini (*75*) have proposed the schematic structure shown below for Schenck's phosphorus.



Two experimental approaches have been used in an attempt to confirm the above postulate. It was hoped that treatment of Schenck's phosphorus with an organometallic compound such as zinc diethyl would effect substitution of the halogen atoms with organic radicals, but apparently no reaction occurred under the experimental conditions applied. The second approach involved an examination of the polymeric materials obtained by the photo-polymerization of solutions of white phosphorus in various solvents, including alkyl and aryl halides, phosphorus tribromide, and some tertiary phosphines.

Table 2. Typical Analyses of Red Phosphorus Polymers

Solvent	Phosphorus (%)	Halogen (%)	Carbon (%)
EtI	72.8	9.4	1.72
BuI	82.5	9.1	3.58
PhI	78.4	5.6	5.54
PBr_3	...	15.4	...

If the red phosphorus obtained when iodobenzene is used as a solvent is boiled with water, the total iodide content is liberated as hydrogen iodide, but the remaining compound still contains carbon. This observation is in agreement with the hypothesis that the aryl groups are actually bound to phosphorus and that these substances are not products of absorption nor are they solid solutions. Further confirmation was obtained from the behavior of the phosphorus polymers which contained alkyl or aryl groups, when they were submitted to oxidation by 5 *N* nitric acid. If the carbon atoms were not attached directly to phosphorus in the polymer, oxidation would give rise to phosphoric acid only. However, substituted phosphonic acids were isolated from such reactions. Decomposition of the phosphorus polymer obtained in the presence of triphenyl phosphine by this method gave nitrophenyl phosphonic acid, isolated as the lead salt. No secondary or tertiary derivatives of phosphine were observed.

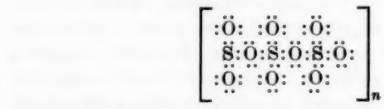
Activation Polymerization of Monomeric Units

Sulfur Trioxide

One of the most interesting inorganic polymerization reactions occurs in the sulfur trioxide system. In the vapor state, this material is largely monomeric, but an equilibrium between cyclic trimers and monomeric units is believed to exist in the liquid state. The physical properties of the vapor and liquid sulfur trioxide do not depend in any way on the state of aggregation of the solid from which they were derived. Three apparently distinct solid modifications of sulfur trioxide have been shown to exist (*77*, *78*).

γ-Sulfur trioxide or the so-called "ice-like" modification can be prepared by condensing sulfur trioxide vapor at a temperature less than 25°C in a receiver free from moisture. This modification melts at 16.8°C, and is considered to consist predominantly of cyclic trimers.

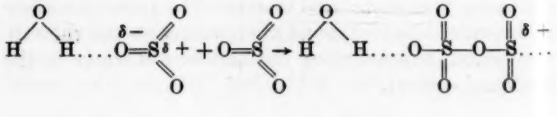
Polymerization of this modification to the β- or "low melting asbestos" form is catalyzed by the presence of water; as little as 225 mg of water is sufficient to polymerize 1 kg of sulfur trioxide (*79*). This partially polymerized material has a fibrous structure, and sulfur trioxide molecules are considered to be linked together in long chains. The chains are probably terminated by the elements of water.

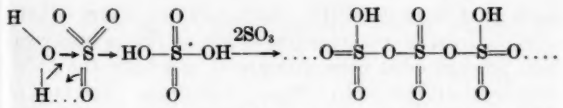


The α-form of sulfur trioxide or the "high melting asbestos" form, with a melting point of 62.2°C, can be prepared from the ice-like modification by repeatedly distilling sulfur trioxide in vacuum, and condensing at liquid air temperature. Measurements of the heats of fusion and vaporization show that α-sulfur trioxide is the most stable form thermodynamically; the β- and γ-forms being only metastable modifications. The structure of α-sulfur trioxide is very similar to that of the β-form except that the chains are further polymerized giving a layer structure.

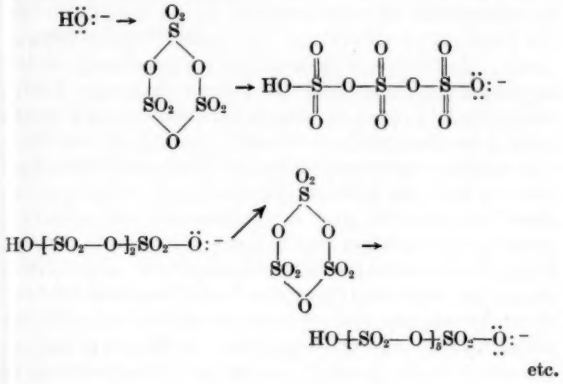
These physically different forms of sulfur trioxide cannot be considered as true allotropes. For instance, the β-modification is apparently only formed in the presence of moisture; from vapor pressure studies, the high melting asbestos form appears to be a mixture. At room temperature, α-sulfur trioxide has a low vapor pressure, but if the temperature is held at 50°C, the pressure increases with time to a limiting value. Now, if vacuum is applied, the vapor pressure can again be reduced to its original value, but with time, the vapor pressure increases again. The melting point of the substance that remains is always higher than that usually ascribed to the α-form; samples melting at temperatures over 90°C have been prepared. In these circumstances, α-sulfur trioxide must be a mixture of at least two components, one being considerably more volatile than the other (*80*).

The polymerization process leading to the high-melting asbestos form has not been studied in any detail, and no mechanism has been proposed. The process leading to the β-modification is initiated by water, probably by the formation of a hydrogen bond with a SO_3 molecule. This would disturb the electrical symmetry on the sulfur atom, creating a more positive center, which would cause polymerization in the presence of excess sulfur trioxide. Two possible mechanisms, based on the initial formation of a hydrogen bond, are shown below.





Another possible mechanism is based on the initial opening of the trimeric sulfur trioxide ring system by nucleophilic attack of a hydroxide ion. A scheme for such a process is shown below.



Phosphonitrilic Derivatives

When phosphorus pentachloride is heated with ammonium chloride, either in the presence of a solvent, such as tetrachloroethane, or as an intimate mixture, partial ammonolysis of the phosphorus pentachloride takes place (*53*, *54*). The resulting product consists of a mixture of polyhomologs with the empirical formula $PNCl_2$. The various members of the series can be separated by fractional distillation at low pressures, followed by recrystallization from suitable solvents (*84*). Discrete compounds in this series have been recognized containing up to eight $PNCl_2$ units. In the analogous phosphonitrilic fluoride series, substances consisting of up to seventeen PNF_2 entities have been detected (*85*). The trimeric and tetrameric compounds are represented by structures in which alternate phosphorus and nitrogen atoms are arranged in six-and-eight membered ring systems, respectively (*86*, *87*). Each phosphorus atom carries two chlorine atoms. Calculations of delocalization energies suggests that the trimeric and tetrameric phosphonitrilic chloride show aromatic character (*88*, *89*).

No structure determinations have been carried out on the higher polyhomologs. Copley (*90*) has suggested that the pentamer, hexamer, and heptamer could be formulated in such a way that the stable six-membered ring systems are retained. This also involves the postulation of condensed ring systems. Krause (*91*) has also presented evidence based on infra-red and ultraviolet absorption studies and the measurement of dipole moments in favor of ring structures for the higher homologs. The trimeric and tetrameric compounds both show strong absorption in the infra-red in the region 1200–1300 cm^{-1} which in each case has been correlated with the presence of a P=N ring system (*92*). A band in this region appears in the spectra of the pentamer, the hexamer, and the heptamer yet it is absent in the spectrum of the highly polymeric compound $(PNCl_2)_x$. There is little variation in the dipole moments throughout the same series, and this is considered evidence against any marked change in the bonding of various homologs.

However, there is an abrupt change in the physical properties of these compounds on passing from the tetramer to the pentamer, e.g., the melting point falls from 123.5°C for the tetramer to 41°C for the pentamer. This evidence is used to support the alternative structural formulation for the higher homologs which is based on chain structures of alternate phosphorus and nitrogen atoms. One difficulty inherent in this postulation is connected with the nature of the terminating groups. The substances are not radicals and it is unlikely that the elements of water are incorporated as the preparation is carried out with rigid exclusion of moisture. Current thought, therefore, favors the view that higher homologs in the series $(PNCl_2)_n$ are in fact cyclic compounds involving large ring systems.

Credence is lent to this by the recent recognition of a series of linear phosphonitrilic compounds end-stopped with the elements of PCl_5, e.g., $PCl_4 \cdot (PNCl_2)_n Cl$ (*82*). These compounds, chlorides of polyimidophosphoric acids, arise when an excess of PCl_5 is employed in the usual preparation or when the cyclic polymers are heated to temperatures above 350°C in the presence of PCl_5. The compounds are very reactive, have low thermal stabilities and are unstable in polar solvents thus making separation of pure compounds exceedingly difficult. A compound $PCl_5 \cdot PNCl_2$, which is probably the first member of this series, has been obtained by heating trimeric phosphonitrilic chloride with three moles of PCl_5 in a sealed tube (*93*). Similarly, the first member of a possible second series of linear derivatives, end-stopped with phosphorus oxytrichloride, i.e., $POCl_3 \cdot PNCl_2$, has been obtained from phosphorus pentachloride and ammonium chloride in the presence of phosphorus oxytrichloride (*94*).

The phosphonitrilic chlorides polymerize when heated, giving products varying from oily liquids and waxes to the so-called "inorganic rubber." The physical state of the product depends on the temperature and time of heating and on whether the original compound was heated in vacuum or under pressure. The elastomeric compound can be obtained by heating either trimeric or tetrameric phosphonitrilic chloride in a sealed tube at approximately 300°C for four hours. Meyer and co-workers (*95*) have estimated that the elastomer consists of chains containing approximately 200 $PNCl_2$ units. The rubber-like compound has a high swelling capacity in aromatic and chlorinated solvents, making probable a certain amount of interlocking between neighboring chains. Recently, Patat and Derst (*96*) have presented evidence that the high polymer consists of statistically entangled rings, individual rings consisting of from 10 to 50 trimeric units, depending on the temperature employed in the polymerization process. Schmitz-Dumont and Braschos (*97*) obtained a mixed fluoro-chloro rubberlike compound when $P_4N_4Cl_4F_4$ was heated under pressure at 300°C. The pure trimeric and tetrameric phosphonitrilic fluorides (*98*) have been prepared recently and been found to polymerize to elastomeric products. Only the rubber-like compound obtained from phosphonitrilic chloride has been examined by X-ray diffraction. A random arrangement is shown when the sample is not under stress, but spacings characteristic of a fiber structure are ob-

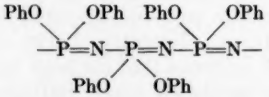
tained when the elastomer is stretched (*95*).

These inorganic rubbers are susceptible to depolymerization by heat. If the temperature of a phosphonitrilic chloride polymer is raised above 350°C, mainly the trimer and tetramer are obtained together with a small amount of the higher oily polyhomologs. Again, the compounds mentioned above all contain active halogen atoms, and are therefore susceptible to hydrolysis by the moisture in the air. After being exposed to a moist atmosphere for a short time, the elastomers lose their rubber-like properties.

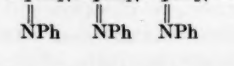
Numerous attempts have been made to replace the active chlorine atoms in the phosphonitrilic chlorides in the hope that the polymeric compounds resulting therefrom would have enhanced stability toward heat and moisture. For example, Dishon (*99*) has obtained the hexa-methoxy and -butoxy derivatives by alcoholysis of the trimeric phosphonitrilic chloride and has shown that these compounds very readily polymerize to water soluble, benzene insoluble resins, even when subjected to vacuum distillation. Decomposition also appears to take place, as the polymeric products show low carbon contents. Trimeric and tetrameric phosphonitrilic chlorides have been found to react in appropriate solvents with alkali metal and ammonium thiocyanates to precipitate insoluble alkali (ammonium) chlorides. The corresponding *iso*-thiocyanates are thus obtained with melting points of 41 and 90°C, respectively (*100*, *101*). These compounds containing the $PN(NCS)_2$ unit polymerize by heating at temperatures above 150°C to rubbery gels. Unfortunately, such elastomers are not stable at higher temperatures; even at room temperature, loss of elasticity is observed in time.

Attempts have also been made to replace the chlorine atoms in polymerized phosphonitrilic chloride by treatment with alcohols (*102*); almost complete removal of chlorine is effected but oxygen rather than alkoxy groups substitute to some extent. Rubbery products are obtained but they show low thermal stability.

Interesting products have been obtained from reactions between phosphonitrilic chloride trimer and compounds such as sodium phenoxide (*103*). Complete substitution of the chlorine atoms takes place and high boiling oily products are produced. The hexaphenoxy derivative does not distil at 320°C under a pressure of a few millimeters of mercury, but prolonged heating at this temperature causes polymerization to a solid material. Chains with the following structure are considered to be formed.



The product obtained by heating acetanilide with phosphonitrilic chloride is a transparent thermo-plastic resin, assumed to contain repeating units of



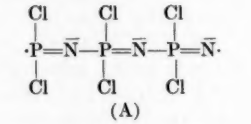
When warm, this product is ductile and may be drawn into fibers.

The literature contains many reports on the preparation of phosphonitrilic derivatives containing groups such as -OH, -OR, $-NH_2$, $-N_2H_3$, -NHR, $-NR_2$, $-C_6H_5$, -SR etc., yet no comparative study of the polymerization processes has been attempted, nor have the products been submitted to critical evaluation. The lack of data on the polymerization of these derivatives is due in some respects to the fact that the actual mechanism of polymerization of the parent chloride has still not been clarified.

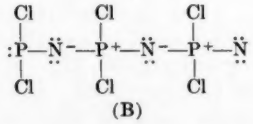
One postulated mechanism for the polymerization of phosphonitrilic chloride involves, as the initiation step, the breaking of trimeric or tetrameric rings by oxygen (*104*). Radicals are believed to be produced, which participate in chain reactions. Such chains are finally terminated by oxygen, which also causes some cross-linking to give products insoluble in organic solvents.

A more recent examination by Patat and Frömbling (*105*) of both the bulk polymerization of trimeric phosphonitrilic chloride and the polymerization in carbon tetrachloride solution has cast some doubts on the validity of the simple picture outlined above. Pure phosphonitrilic chloride trimer can be polymerized by heat alone, but no aggregation occurs in carbon tetrachloride solution in the absence of oxygen. Addition of carbon tetrachloride to material undergoing bulk polymerization causes complete inhibition of the reaction, but this effect can be overcome by the addition of a trace of oxygen.

A reaction scheme has been worked out on the basis of these results. For bulk polymerization, thermal unimolecular initiation is assumed, giving first a diradical linear chain (A). The propagation reaction from such an activated species would be similar to that occurring in vinyl polymerization processes. The activated monomer could be considered to be a mesomeric form (B) of the diradical.

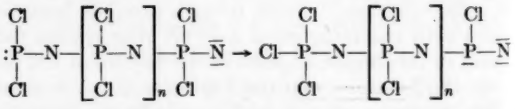


(A)



(B)

Under these circumstances, the chain could be propagated by interaction between the pair of electrons on an end phosphorus atom with an electron-pair-deficient end nitrogen atom, or by a nucleophilic attack of such a species upon the ring structure to bring about heterolytic fission of the latter. This would then constitute the propagation reaction. The kinetics of the propagation reaction would therefore be bimolecular. Two possibilities exist for a unimolecular chain termination: (*a*) small chains may close to give cyclic structures; (*b*) a chlorine atom may migrate to an end phosphorus atom as shown below.



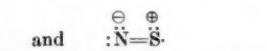
Konecny and Douglas (*106*) have found that the rate of the bulk polymerization of the trimer per se *in vac uo*

is very slow at 211°C. However, a large number of organic compounds and metals catalyze the polymerization reaction. The catalytically active compounds include ethers, ketones, alcohols, and organic acids, and are characterized by their ability to react with the phosphonitrilic compound to produce hydrogen chloride. Benzene and carbon tetrachloride do not appear to react with the $PNCl_2$ and have no pronounced effect on the polymerization rate.

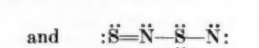
Tetrasulfur Tetranitride

The molecule of tetrasulfur tetranitride consists of an eight-membered ring system of alternate nitrogen and sulfur atoms. This substance can be related generically to the molecules of rhombic sulfur, tetrasulfur tetrimide, and heptasulfurimide (*58*). The usual method of preparation entails treatment of a solution of a sulfur chloride with ammonia gas. It is also formed when sulfur and liquid ammonia are allowed to react at room temperature. When tetrasulfur tetranitride is heated in high vacuum to 300°C and the vapors are condensed in liquid air, a white volatile product, soluble in many organic solvents, is obtained. Cryoscopy has established the formula as $(NS)_2$. This product is unstable except at low temperatures; on standing at room temperature, it passes over into a brass-colored, insoluble polymer with the formula $(NS)_n$. In the presence of moist air, tetrasulfur tetranitride accompanies the formation of polysulfur nitride (*107*).

The monomeric form, thionitrosyl (NS), is unknown but could be considered analogous to nitric oxide. The monomer can be represented by two radical structures, i.e.,



which, if capable of existence, would lead to the dimer, represented by the following structures.



(A) (B)

Two mechanisms, then, are possible to account for the further polymerization. Structure (A) has a butadiene-like arrangement which, in the presence of molecular oxygen or other radical initiator, could be activated to facilitate continuous 1,4 addition to give the high polymer. The alternative mechanism (see structure B) involves donation of a pair of electrons from an end sulfur atom to an end nitrogen. This process could stop at a dimeric state to give S_4N_4 by cyclization, i.e.,

but if it were continuous the long chain polymer would result.

A discussion of the formation of polymeric materials by coordination processes will be the basis of the final paper in this series.

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GUEST AUTHOR
A. J. Poë
Imperial College
of Science and
Technology
London, England

Textbook Errors, 23

Atomic Masses, Binding Energies, and Isobaric Stability

Increase in binding energy is often given as a measure of the tendency of a spontaneous nuclear reaction to proceed. This is correct in certain cases, e.g., α-decay and fission, but is clearly incorrect for isobaric decay (i.e., β^--, β^+-emission and electron capture) to which it is sometimes applied in textbooks.[1] The basic and generally applicable criterion is that there should be a decrease in mass during the reaction. Because of the difference in mass between the neutron and the hydrogen atom the binding energy criterion is equivalent to this only when the neutron: proton ratio remains constant during the reaction.

The difference between the two criteria can be quite appreciable and can lead to qualitatively erroneous predictions of the direction of decay and to quantitative errors in estimating the energy released which are much larger than experimental errors.

In the following we shall review the basic definitions involved and the methods of estimating isobaric decay energies and also give an example showing the difference between the correct and the incorrect approach.

Mass and Binding Energy Conditions for Isobaric Decay

A nucleus can be characterized by its mass number A and charge Z, both of which are integers. In an isobaric series A is constant and Z is variable. For our purpose it is convenient to consider the mass of the *atom*, denoted by $M_{Z,A}$, together with the masses of the hydrogen atom, the neutron and the electron, denoted by M_H, M_n, and M_e, respectively.

In a spontaneous nuclear event such as β^--decay the only source of kinetic energy for the emission of the β^--particle must lie within the system itself. Because of the equivalence and interconvertibility of mass and energy this energy is provided at the expense of mass, i.e., the mass of the products is less than the mass of the reactants. Therefore, for the three types of isobaric decay the mass conditions, expressed in atomic mass units, are:[2]

β^--emission:	$M_{Z,A} > M_{Z+1,A}$
Electron capture:	$M_{Z+1,A} > M_{Z,A}$
β^+-emission:	$M_{Z+1,A} > M_{Z,A} + 2M_e$

Now the binding energy of a nucleus is the difference between the total mass of the separated nuclear constituents (protons and neutrons) and its actual mass. It can be considered as the energy released during the hypothetical formation of the nucleus from its constituents and is given by:

$$B_{Z,A} = ZM_H + (A - Z)M_n - M_{Z,A}$$

where the relatively much smaller electron binding energy differences are neglected. The mass change in isobaric decay is related to the binding energy change as follows:

$$M_{Z+1,A} - M_{Z,A} = B_{Z,A} - B_{Z+1,A} - (M_n - M_H)$$

The mass difference between the hydrogen atom and the neutron is well known and can be expressed in units of millions of electron volts as:

$$M_n - M_H = 0.78 \text{ Mev}$$

The binding energy conditions for isobaric decay are therefore:

β^--emission:	$B_{Z+1,A} > B_{Z,A} - 0.78$ Mev
Electron capture:	$B_{Z,A} > B_{Z+1,A} + 0.78$ Mev
β^+-emission:	$B_{Z,A} > B_{Z+1,A} + 2M_e + 0.78$ Mev

Thus β^--emission is energetically possible even when the binding energy *decreases* by up to 0.78 Mev. Conversely, for electron capture the binding energy must increase by more than 0.78 Mev. For β^+ emission this excess is increased by $2M_e$, or 1.01 Mev, the energy equivalent of the sum of the rest masses of the positron and the excess orbital electron.

Calculation of Isobaric Decay Energies

The calculation of isobaric decay energies is possible using a semi-empirical mass equation, quoted in most nuclear physics and radiochemical textbooks, which can be written:

$$M_{Z,A} = ZM_H + (A - Z)M_n - a_1A + a_2A^{2/3} + a_3Z^2A^{-1/3} + a_4(\tfrac{1}{2}A - Z)^2A^{-1} \pm \delta \quad (1)$$

where δ is a term the value of which depends on whether A is odd or even, and the constants a_1, a_2, a_3, and a_4 can be evaluated semiempirically. A critical summary of available values is given by Evans.[3] "Average" values, valid over a wide range of A, are necessarily less precise than "local" values, of more limited validity, obtained by reference to experimental data over only a small range of A.

Suggestions of material suitable for this column and guest columns suitable for publication directly are eagerly solicited. They should be sent with as many details as possible, and particularly with references to modern textbooks, to Karol J. Mysels, Department of Chemistry, University of Southern California, Los Angeles 7, California.

[1] Since the purpose of this column is to prevent the spread and continuation of errors and not the evaluation of individual texts, the source of errors discussed will not be cited. The error must occur in at least two independent standard books to be presented.

[2] Moon, P. B., "Artificial Radioactivity," The University Press, Cambridge, England, 1949, p. 36.

[3] Evans, R. D., "The Atomic Nucleus," McGraw-Hill Book Co., Inc., New York, 1955, p. 383.

The variation of mass or binding energy with varying A and Z can be represented by a contour diagram called a nuclear mass, or energy, surface and this takes the form of a valley running along a line with $A\text{-}Z \geqslant Z$, the stable nuclides lying at the bottom. For an isobaric series with a constant but odd value of A, corresponding to a vertical section across the valley, $\delta \approx 0$ and the equation predicts the section to be parabolic. When A is even δ is not negligible and two parabolas are obtained, separated vertically by $2\,\delta$, with nuclides of even Z lying on the lower curve and those with odd Z on the higher. The value of Z at the minimum of each parabola is clearly different for mass and binding energy curves. Since relative isobaric stability is more relevant when considering the occurrence of stable isobars in nature, than stability relative to total disintegration into their constituents, the mass, and not the binding energy, surface should be used. When A is odd the mass parabola can be written:

$$M_{Z,A} = M_{Z_0,A} + {}^1/_2 B_A (Z - Z_0)^2 \qquad (2)$$

where Z_0 is the value, not necessarily integral, of Z at the minimum of the parabola and B_A is the curvature. The minimum of the corresponding binding energy curve is at a Z value $0.78/B_A$ units smaller than Z_0. B_A varies from ~ 3 to ~ 1 as A increases from 60 to 180[4], and is the same for corresponding mass and binding energy curves and even average values are sufficiently accurate for mass calculations. However, since the mass depends on $(Z\text{-}Z_0)^2$, inaccuracy in Z_0 leads to large errors in the calculated masses. On using average values of the parameters the uncertainty in Z_0 is $\pm 3.6/B_A$ but when local values are used the uncertainty is less, calculated mass differences become more precise, and their 0.78 Mev difference from corresponding binding energy differences becomes significant.

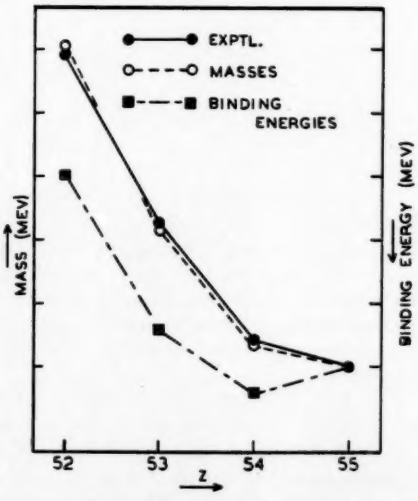

Figure 1. Comparison of the best calculated masses and binding energies for $A = 133$ with experimental energy changes, all plotted relative to stable $_{55}Cs^{133}$.

Calculated values of the mass differences for $A = 133$ are listed in the table together with corresponding binding energy differences in brackets. The predictions based on masses become progressively closer to the experimental results as the parameters become more local while those based on binding energies show no such improvement. The best predictions were obtained using "optimum values" of the parameters, i.e., $B_A = 1.43$ (local value given by Coryell[4]) and $Z_0 = 54.75$ (obtained as the average of the Z_0 values calculated for $A = 131$ and 135 using local values of B_A and accurate experimental values[5] of the total decay energy for I^{131} and Xe^{135} together with equation (2)).

Comparison of Calculated Mass and Binding Energy Changes with Experimental Decay Energies $A = 133$

	Calculated mass change (Mev) (corresponding binding energy changes in brackets)			
$Z \rightarrow Z\pm1$	From average parameters[3]	From local parameters[4]	From optimum parameters†	Total decay energy (Exptl.[5])
52 → 53	4.54 (3.76)	3.49 (2.71)	3.22 (2.44)	3.0
53 → 54	3.17 (2.39)	2.07 (1.29)	1.79 (1.01)	1.83
54 → 55	1.79 (1.01)	0.64 (−0.14)	0.36 (−0.42)	0.43
56 → 55	−0.41 (0.37)	0.78 (1.56)	1.07 (1.85)	>0.44
57 → 56	0.96 (1.74)	2.21 (2.99)	2.50 (3.28)	≥2.2
58 → 57	2.34 (3.12)	3.64 (4.42)	3.93 (4.71)	≥2.3

† I.e., local curvature from Coryell.[4] Z_0 by averaging Z_0 values calculated for $A = 131$ and 135 using experimental decay energies[5] for I^{131} and Xe^{135}.

The predictions based on the optimum parameters are compared with the accurately known experimental values in the graph. For comparative purposes the masses and binding energies are arbitrarily plotted relative to a common point at $Z = 55$ (stable Cs^{133}) and the *gradients* of the lines joining the points represent the predicted energy changes. The experimental energy changes, also referred to $Z = 55$, lie very close to the mass differences while the binding energy changes are quantitatively and even qualitatively different, the binding energy criterion predicting $_{54}Xe^{133}$ to be the stable isobar.

As more accurate equations for calculating atomic masses become available, and as more experimental data are obtained, examples illustrating the logical error of using binding energy differences will become still more plentiful.

Acknowledgment

The author is indebted to Professor Karol J. Mysels for his advice and many helpful suggestions during the preparation of this paper.

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Wesley W. Wendlandt
Texas Technological College
Lubbock, Texas

An Inexpensive Differential Thermal Analysis Apparatus

Although differential thermal analysis (DTA) has been known since 1887 (*3*), only recently has it assumed much importance to the analytical chemist. By use of this technique, the qualitative identification of a compound is possible by determining the temperatures at which endothermic (endotherm) or exothermic (exotherm) reactions take place as the substance is heated. Previous studies of this type, to mention but a few, consisted of the identification of metal nitrates and perchlorates (*2*), lubricating greases (*1*), polyglucosans (*6*), and starches and other organic compounds (*4*, *5*). However, much fruitful work lies ahead in this interesting area of investigation.

Many authors have described the instrumentation for DTA (*8*). The apparatus usually consists of a furnace and sample holder, a furnace temperature controller, an electronic or other type of recording device, and a low-level dc amplifier. To the small laboratory, the cost of such an apparatus consisting of the above components is usually prohibitive. In an effort to reduce this financial barrier, an inexpensive DTA apparatus that performs reasonably well in the temperature range from ambient to 800°C was constructed.

The DTA apparatus consists of an easily built furnace and stainless steel sample holder; a motor-driven variable transformer to control the temperature of the furnace; and an inexpensive strip-chart microvolt recorder made from an illuminated D'Arsonval type galvanometer. The operation of the apparatus is completely automatic.

Recorder. A schematic diagram of the recorder is given in Figure 1. The recorder consists of a Leeds and Northrup D'Arsonval type galvanometer, Cat. No. 2430-C, 0.0029 μ amp/mm, in which the reflected beam of light falls on a Type 920 twin-cathode photocell. The unbalance from the photocell cathodes is fed into two Type 2051 thyratron tubes which are resistance coupled to the Barber-Coleman, Type OYAZ-433, reversible pen drive motor. The thyratron circuit used in the recorder has been described by Wilkie (*10*) and is a modification of the original circuit proposed by Pompeo and Penther (*7*).

The chart drive assembly was built from $^1/_8$-in. thick aluminum sheet while the chart gear drive mechanism was cut from an appropriate size aluminum rod. The chart drive motor was a 2-rph synchronous motor made by the Cramer Controls Corp., Centerbrook, Conn. It was equipped with a two-way friction clutch which allowed manual movement of the paper to be made in either direction. Using a motor of this speed, the chart paper travel was approximately 6 in. per hour. Other chart speeds could be obtained by changing the inexpensive drive motor. Standard 5-in. wide Varian

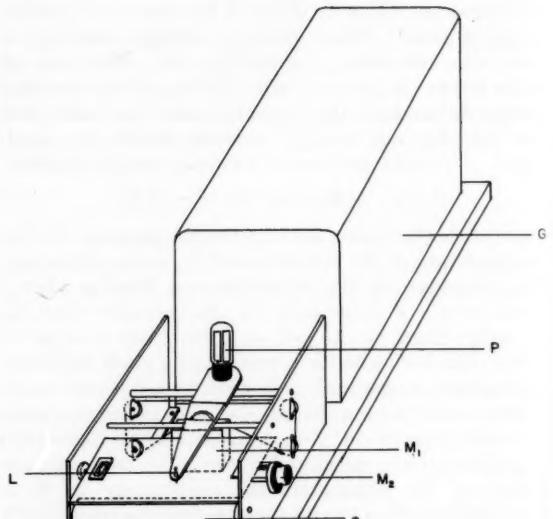

Figure 1. Schematic diagram of the recorder: G. Galvanometer; P. Type 920 photocell; M_1. Pen drive motor; M_2. Chart drive motor; C. Chart paper roll; L. Leroy Type 000 lettering pen.

Associates chart paper was used in the recorder.

The input to the galvanometer was connected to a ten-turn, 100-ohm Micropot which acted as a voltage divider from the differential thermocouples. Since the galvanometer was quite sensitive, an expensive dc amplifier was eliminated because for most purposes, the galvanometer response was adequate. Actually, in most cases, the Micropot was adjusted to take off 80% of the emf generated by the differential thermocouples.

The entire recorder unit, except for the chart drive assembly, was enclosed in a light-tight wooden box.

Furnace. The furnace is illustrated in Figure 2. The sample holder, *A*, as well as the furnace tube, were made from Type 303 stainless steel. Dimensions of the sample holder were 3.0 in. × 1.2 in, with the 10.0-in. long furnace tube of a slightly larger inner diameter to permit the holder to fit snugly.

The furnace tube was insulated with several layers of asbestos paper and wound with 10 ft of 0.020-in. Nichrome wire (1.62 ohms per ft). A 4-in. aluminum tube formed the outer case of the furnace, using asbestos wool as the internal insulation.

The thermocouples were made from 28-gauge platinum and 28-gauge 90% platinum–10% rhodium alloy wire. Their location in the sample holder is shown in *B* of Figure 2. The thermocouple leads were held in

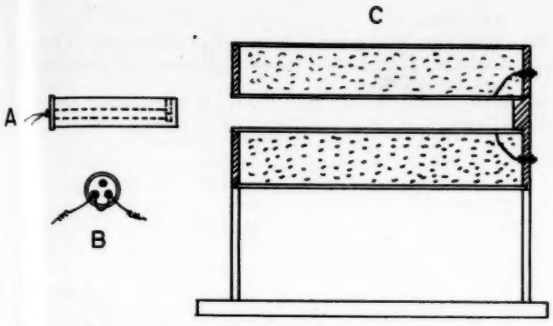

Figure 2. Furnace assembly: A. Sample holder, side view; B. Sample holder, end view; C. Furnace, side view.

porcelain insulators and cemented into the two lower holes in the sample holder with Sauereisen No. 1 cement. The upper hole in the sample block contained an iron-Constantan thermocouple which was used to measure the furnace temperature.

The differential thermocouple beads terminated in the sample chambers which were 0.25 in. in diameter × 0.625 in. deep. The samples were heated using a "sandwich" type packing which consisted of a layer of ignited alumina, a layer of sample (in intimate contact with the thermocouple bead), and another layer of alumina. Using this method, adequate recorder response was obtained from samples ranging in weight from 100–350 mg.

Furnace Temperature Controller. The temperature controller consisted of a 0–135-v Powerstat rotated by a 1/6-rph synchronous motor containing a two-way friction clutch. Starting at an initial Powerstat voltage of 40 v, the furnace heating rate curve in Figure 3 was obtained. As can be seen, the heating rate was linear from about 50 to 750°C, at about 10.5°C per minute.

Results. To illustrate the operation of the apparatus, the thermograms of magnesium nitrate 6-hydrate and barium nitrate are given in Figure 4. These two compounds were chosen because the magnesium salt is decomposed in the low temperature range (up to 500°C) while the barium salt decomposes in the high temperature range (above 500°C). Gordon and Campbell (*2*) have previously studied these two compounds but a rigorous comparison cannot be made because of the different type of furnace sample holder and recorder that was used.

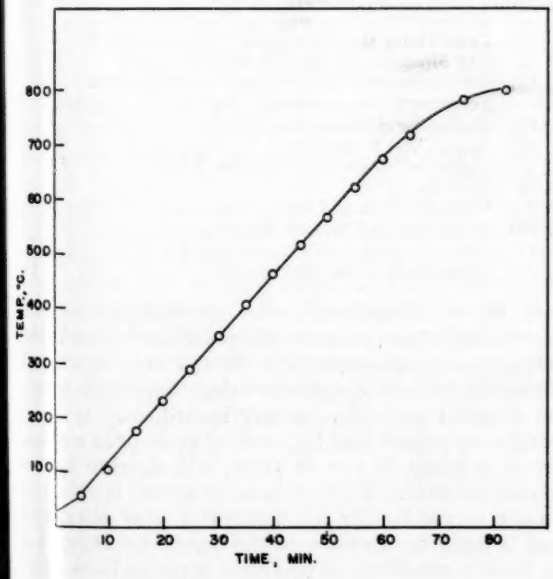

Figure 3. Heating rate curve of furnace.

Magnesium nitrate 6-hydrate exhibited four endotherms, the temperature of the curve maximas being 90°, 110°, 190°, and 450°C, respectively. Fusion of the salt is revealed by the 110°C endotherm while immediately following this is the dehydration endotherm at 190°C. The decomposition of anhydrous magnesium nitrate to magnesium oxide occurred at the 450° endotherm. Origin of the 90°C endotherm is not known; it could possibly represent a crystalline phase transition.

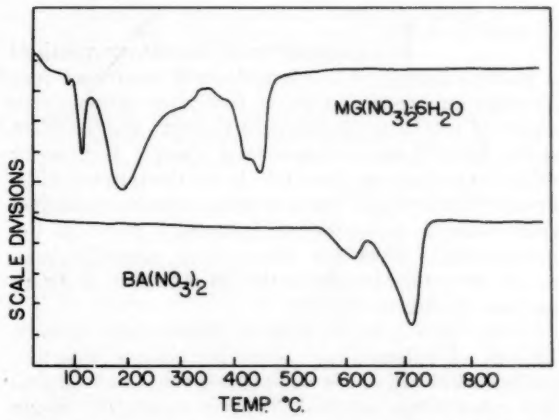

Figure 4. Thermograms of magnesium nitrate 6-hydrate and barium nitrate. Sample sizes 0.281 g and 0.094 g, respectively. Sensitivity of 0.80.

The DTA thermogram agrees fairly well with the reactions found from a weight loss study using a thermobalance (*9*). Again, it is not possible to make a rigorous comparison because of the different conditions in the furnace chamber and also the different heating rates employed.

The high temperature thermal decomposition of barium nitrate gave two endotherms; one at 670°C, the other at 710°C. The endotherms are due to the decomposition of nitrate to the metal oxide. Agreement with previous studies (*2*) is excellent for the 710°C endotherm but the 670°C peak is somewhat high.

The apparatus, as described, has been in operation in this laboratory for several months. Entire cost of the unit, excluding labor, was about $250.

Acknowledgment

It is a pleasure to acknowledge the assistance of Warner Kendall and John L. Bear in construction and assembly of the apparatus.

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Howard Nechamkin
Pratt Institute,
School of Engineering
Brooklyn 5, New York

An Approach to Laboratory Instruction in General Chemistry

The efficient use of laboratory meetings in general chemistry has long been a matter of considerable importance at Pratt Institute. Simple repetition of reactions described in the text and/or those which have been demonstrated during lecture or recitation periods, we have felt, is not the purpose to be served. There have been several articles published which describe research-type laboratory work on the undergraduate level but these have generally been meant for students above the freshman level or in qualitative analysis (*1–11*).

A step in the direction of use of the laboratory toward the end of encouraging scientific thinking and the application of principles was made when a new laboratory manual was adopted. This manual (*12*) is one which emphasizes precision of measurement and exposure to a wide variety of laboratory techniques and requires extensive and careful handling of data in arriving at report results. During the past two years a new and very successful approach has been adopted.

First Semester

The first semester of general chemistry laboratory is now devoted exclusively to acquainting the students with the facilities available in the laboratory and the various end-results which may be achieved by their use. Toward this end, quantitative experiments are carefully chosen from the manual so that in this semester as many different laboratory techniques as are feasible are covered.

A novel feature of the work of this semester is that the students are often told exactly what the results of their experiments are expected to be. They also are not graded on the basis of the results which they obtain. They are instead expected to keep laboratory notebooks which are always up-to-date and contain a careful record of their work, observations, calculations, etc. Most interesting in these notebooks is the section for each experiment where the student attempts to account for the deviations of his results from those which are expected. It is here where we can see exposed his ability to think and analyze critically by observing the student's evaluation of his techniques and results.

By the time the semester has been completed we feel that even the mediocre student realizes that the laboratory is not the place where blank spaces for recording colors of precipitates, etc., are to be filled in. It is instead a place where the tools of science are put to use in examining and exploring the behavior of matter and energy, where the laws of science are tested, and where the only authority is the datum.

In the course of the semester the student becomes acquainted with the standard techniques involved in gravimetric, volumetric, colorimetric, and chromatographic procedures. He also makes melting point and boiling point determinations, works with gases, and performs distillations, extractions, crystallizations, and numerous other important laboratory activities. In this semester he is also presented with a set of library problems which are designed to acquaint him with the important periodicals and other library facilities and procedures.

Examples of some experiments which are done in this semester include such exercises as:

(1) Determining the Value of the Gas Constant, R.
(2) The Molecular Weight of a Volatile Liquid.
(3) Concentration as It Influences Reaction Rate.
(4) Percentage Composition of a Salt.
(5) Formation of Magnesium Nitride.
(6) Amino Acid Separation.
(7) Molecular Weight from Solution Data.
(8) Polarimetry.
(9) Cooling Curves and Phase Diagrams.
(10) Metallurgy and Metallic Properties.
(11) Determination of CO_2 in a Carbonate.
(12) Preparation of Barium Chloride.

At the very beginning of the first semester the student is told of the purposes which his laboratory work will serve and is presented with the challenge which will come with the second semester—that of actual research. He is asked to begin thinking immediately of some problem or project that he, working alone or as a member of a group of two or three, will develop in the second semester. Each student, or group, is asked to submit to the faculty for approval a brief outline of such a project. In some cases projects are suggested by faculty members. The actual work on these projects is the work performed during the laboratory

sessions of the second semester.

At the start of the second semester each student is handed a copy of an announcement regarding reports on his work during the term which reads as follows:

Procedure for Chemistry 102 Laboratory

(1) Each student individually must check in with his instructor at the beginning of each assigned laboratory period.

(2) A bi-weekly progress report will be submitted by each group. Elegance of language and appearance of the report will enter into its evaluation, as well as the technical contents. These reports are to be turned in to the secretary of the Department of Chemistry.

(3) The form of each report must be such that the following items are clearly indicated:

(*a*) Title of the project.
(*b*) Names of students working on the project.
(*c*) A summary of the work done on the project during the two-week period covered by this particular report.
(*d*) Conclusions and discussion.
(*e*) Plans for further work.

(4) Make copies of these progress reports for yourselves. The reports will *not* be returned.

(5) One week before the end of the semester a final report will be due. This report will include, in addition to the conclusions and a complete collation and summation of all previous progress reports, an extensive bibliography consisting of detailed and specific pertinent citations.

(6) At unspecified times, members of the Department of Chemistry will, at random, select individual students to present to them a short but formal oral report on the goals, techniques, and current status of the project. This step is taken to insure full cooperation by all members of the group in the development of the various projects.

Considering the fact that this is a program followed by all of our students, not just honor students, the results have been gratifying indeed. The enthusiasm and interest which the students show in their work is all, and even more, than what we hoped it would be. It is important, too, that there are no longer complaints that the library is not being used enough by the students. The faculty, too, feel that the laboratory meetings have become challenging sessions although quite demanding of time and energy. It is not at all unusual for us to be asked by students to be permitted to work overtime on their problems. In all, it appears to be a very active and intellectually healthy atmosphere in which to work and to learn.

At first there was some misgiving about even starting a program of this type because of the expenses that would certainly be involved in obtaining special equipment and reagents for the numerous projects which would be in operation. An actual accounting of expenses involved clearly show that, if there is a trend at all, it is indeed less expensive to run the course in this way than it had been previous to its inception. We also expect that in subsequent years the cost will be even less because of the fact that much of the materials purchased during the first years will remain useful for further project work in the future.

Another aspect of the program is that laboratory periods are best taught by faculty members assisted, perhaps, by senior students. This helps to raise the laboratory meetings from the unjustified low level in which they so often are found when laboratory instruction is done by graduate students, the least qualified of the faculty personnel, etc. It has been found that a faculty member can easily handle three or four laboratory classes of this type a term, each numbering about 25 students, with no hardship at all.

For those who might like to try experimenting with the approach which we are using, the following is a partial list of the titles of some typical projects:

Resolution of the *cis* form of dichlorobis(ethylenediamino) cobalt III chloride.
Determination of the relative rate of tooth decay when teeth are protected by various dentifrices.
Efficiency of alloy-plating baths.
Separation of tantalum from tantalite.
Analysis and evaluation of commercial gasoline additives.
Construction and operation of a cloud chamber.
Association of HCl in various solvents.
Comparison of three methods of acetylating aniline.
Determination of the initial velocity of radioactive emissions.
Solubility curve for butanol-HCl (aq).
Preparation of hexammine cobalt III chloride.
Gas chromatography.
Preparation and properties of several alkyd polymers.
Comparison of several methods for measuring gas densities.
Preparation of hydrogen persulfide and its reaction with benzaldehyde.
Variation of components as they affect the properties of lipsticks.

Acknowledgment

The author would like to recognize and to acknowledge the invaluable assistance and suggestions for developing this approach to the general chemistry laboratory of Professors John M. O'Gorman and John J. McClarnon and of Mr. Marvin Charton, all of the Department of Chemistry of Pratt Institute. It is hoped that others who use the approach will communicate with the author so that a large set of good projects can be accumulated and the philosophy of the educational technique be evaluated.

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Andrew K. Galwey
The Queen's University
of Belfast
Belfast, Northern Ireland

Thermal Decomposition of $KMnO_4$

A high vacuum experiment for students

The experiment described in this article illustrates some of the manipulations used in high vacuum studies and at the same time demonstrates the application of vacuum technique to the study of reactions occurring in the solid phase. It was designed as an experiment in the practical physical chemistry course for final year (honors chemistry) university students.

The decomposition of a solid was selected as a suitable topic since developments in this field are resulting from the use of vacuum techniques and also since a relatively simple vacuum train may be used to follow the reaction kinetics. The experiment provides a practical investigation of a reaction which is not of a simple kinetic order but obeys a rate equation characteristic of many solid phase decompositions. Rates of decomposition of solids are not in general directly proportional to a power of the concentration of the unreacted species (such as is often the case for reactions occurring in the homogenous phase) but are more often proportional to the area of the interface between product and undecomposed salt. This interface is the region of strain in which the reaction actually takes place.

Potassium permanganate was selected as a suitable substance for the experiment. The kinetics of the thermal decomposition of potassium permanganate have been studied by Prout and Tompkins.[1]

The only disadvantage of potassium permanganate is that decomposition nuclei cannot be directly observed (these nuclei are the coherent particles of product formed in the surfaces of a decomposing crystal; they grow by progression of the product/reactant interface through the undecomposed crystal as the reaction proceeds).

The observation of decomposition nuclei on a whole crystal of ammonium perchlorate heated *in vacuo* at 220°C is an interesting second part to the experiment; a set of photographs showing the growth of decomposition nuclei in a crystal of ammonium perchlorate and details of the method of preparation of crystals have been given by Bircumshaw and Newman.[2] Care should be taken to ensure that the corrosive product gases (chlorine, etc.) do not come in contact with the mercury of the McLeod gauge.

The Apparatus

The apparatus is shown diagrammatically in Figure 1. The

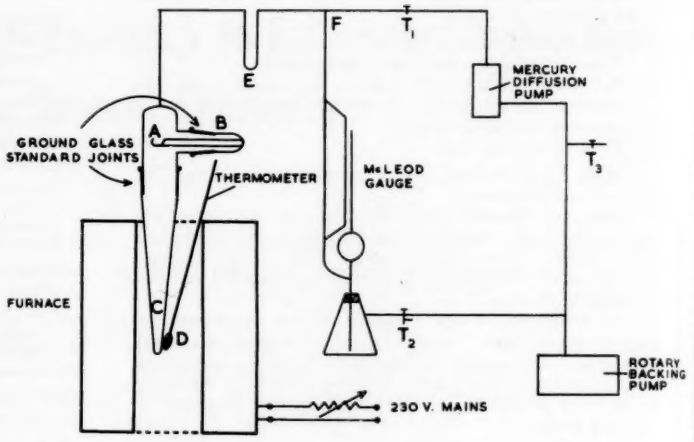

Figure 1. Diagrammatic sketch of apparatus.

crystal to be decomposed is held during evacuation of the apparatus in the spoon (*A*) attached to the ground glass joint (*B*) which, on rotation, drops the crystal into the reaction zone (*C*) situated in the electric furnace. The temperature of the crystal during decomposition is measured by the thermometer clamped with the bulb (*D*) touching the wall of the reaction zone. Both the reaction vessel and the glass spoon may be detached from the apparatus at the ground glass joints (lubricated with silicone grease to avoid melting by heating from the furnace). The electric furnace heaters are supplied from 230-v mains through a variable resistance which is manually adjusted during each experiment to maintain constant reaction zone temperature. It was found that automatic furnace temperature control was not necessary. Constancy of temperature is improved by inserting a plug in the bottom of the furnace and by packing the top, around the reaction vessel, with asbestos wool.

The product gases fill the apparatus to the stop-cock T_1, condensible gases being removed in the trap *E* immersed in liquid nitrogen to a constant level maintained by frequent small additions during the course of a decomposition. Pressure in the constant volume system was measured with the McLeod gauge (capillary diameter 1.5 mm; bulb volume 40 cc).

5-mm diameter glass tubing was used throughout the constant volume system and for the connection to the diffusion pump; no glass/rubber joints were used on the high vacuum side. 5-mm diameter rubber pressure tubing was used for the connection between backing and diffusion pump. Care should be taken to ensure that the point *F* is sufficiently high, so that flooding of the apparatus is prevented if atmospheric pressure of air should be inadvertently admitted to the McLeod gauge mercury reservoir.

The Experiment

At the start of an experiment the reaction vessel is cleaned out (dilute potassium iodide/dilute sulfuric acid solution), dried, and reconnected to the apparatus. A crystal of potassium permanganate (see footnote 1 for method of preparation) is placed in the spoon. A suitable weight of crystal is 4–5 mg for an apparatus of 200-cc volume having a McLeod gauge of the dimensions given above. The apparatus is evacuated with stopcocks T_1 and

[1] Prout and Tompkins, *Trans. Far. Soc.*, **40**, 488 (1944).
[2] Bircumshaw and Newman, *Proc. Roy. Soc.*, **A 227**, 115–32; 228–41 (1955).

T_2 open, T_3 closed. T_2 is closed when a vacuum has been attained and the diffusion pump and furnace heaters are switched on; the apparatus is thoroughly evacuated and the furnace temperature allowed to reach equilibrium in the range 210–220°C at constant temperature (±1°C) by manual adjustment of the power supply.

The McLeod gauge is read in the usual way; a calibration curve, giving a plot of pressure in the constant volume against difference in height (h) of mercury in the two limbs when the mercury in the open limb is brought level with the seal of the closed limb, is provided. The open tube of the two-way stopcock T_2 is connected to a 5-cm length of pressure tubing having a small slit in one side and blocked at the open end; careful bending of this tube enables the rise of mercury in the gauge to be accurately controlled. Air in the McLeod gauge reservoir may be evacuated by the rotary pump; when testing outgassing at the start of a run, T_1 should be closed until this air has been pumped away.

When a sufficiently low rate of pressure rise in the apparatus has been attained (pressure less than 5×10^{-4} mm after T_1 has been closed 10 min.) and the furnace temperature has reached a suitable constant value, a liquid nitrogen trap is put around E, T_1 is closed and the crystal is dropped into the reaction zone. Pressure readings are taken every two or every three minutes until the rate of reaction is very slow; the apparatus is then allowed to stand 2–3 hrs before the final pressure (P_f) readings are taken, corresponding to completion of reaction. (The instant at which the mercury isolates the gas in the McLeod gauge bulb from that in the reaction vessel is the time at which the reading is made.)

The diffusion pump should be turned off when the crystal has been dropped. On completion of the reaction, when the pressure change with time due to reaction is zero, the liquid air trap is removed, T_1 and T_2 opened to the pumps, and then the backing pump is switched off and T_3 is simultaneously opened to the atmosphere.

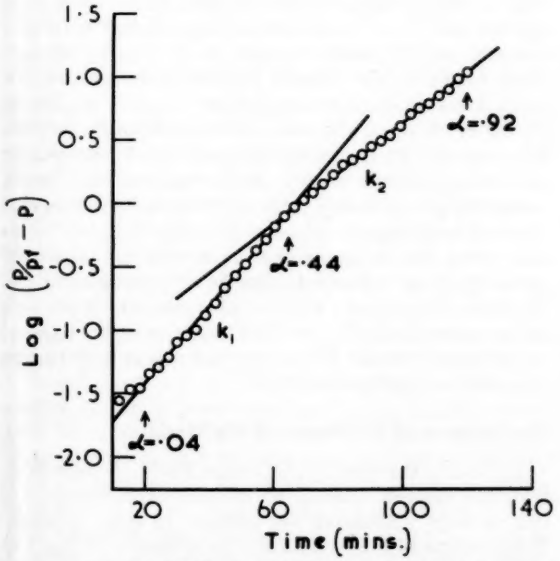

Figure 2. Plot of log $(P/P_f - P)$ against time for the isothermal decomposition of a single crystal of potassium permanganate in constant volume. $\alpha = P/P_f$ = fractional decomposition.

A plot of pressure against time for the isothermal decomposition of a crystal of potassium permanganate in a constant volume gives a sigmoid-shaped curve typical of many solid phase decompositions. Reaction is at first slow but accelerates to a maximum value after which it becomes deceleratory, finally ceasing altogether. The reaction has been found to fit the kinetic law

$$\log (P/P_f - P) = kt + c$$

where P is the pressure at time t; this equation has become known as the "Prout-Tompkins" equation. In the decomposition of potassium permanganate two rate constants hold over different ranges of fractional decomposition. The equation has been derived theoretically from a model whereby reaction proceeds in strained regions of the crystal which either were present

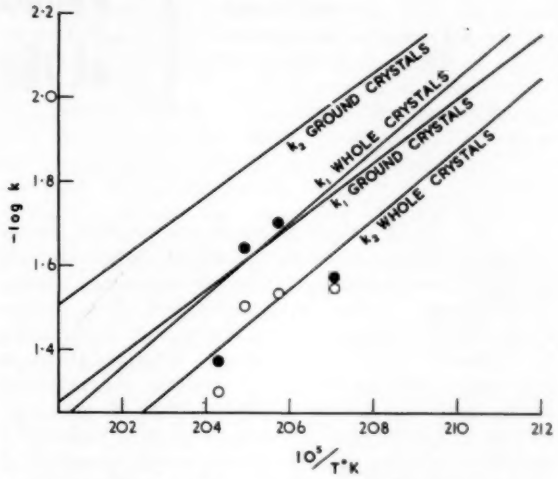

Figure 3. Arrhenius plot for thermal decomposition of crystals of potassium permanganate. —— From results given by Prout and Tompkins. ○ Acceleratory region rate constants (k_1) found by students using the apparatus described. ● Decay region rate constants (k_2) found by students using the apparatus described.

in the lattice originally or were induced as result of reaction in a manner which is comparable to a branching chain reaction; for further details the reader is referred to the original paper[1] or to a more recent survey of the field by Jacobs and Tompkins.[3]

Figure 2 shows a plot of log $(P/P_f - P)$ against time from readings taken by a student who had no previous experience in vacuum techniques, working under normal class conditions; the plot shows different rate constants holding over the different ranges of fractional decomposition (P/P_f). Rate constants found by pairs of students, working together, are shown on the Arrhenius plots, Figure 3, compared with those of Prout and Tompkins. Bearing in mind the irreproducibility of decomposition kinetics sometimes found between different batches of crystals and the slight deviations from linearity on the Prout-Tompkins plot which makes the accurate determination of rate constants difficult, and realizing that the students had not previously used high vacuum techniques, the agreement between the two sets of rate constants is considered most satisfactory. Acceleratory region rate constants may be expected to be sensitive to the batch of crystals used and, as a consequence, the Arrhenius plot may be shifted, so accounting for the results on Figure 3 where all the values of log k_1 found here are lower than those reported by Prout and Tompkins.

Acknowledgment

The author wishes to thank J. Stewart for permission to use the results presented in Figure 2.

[3] JACOBS AND TOMPKINS, "Chemistry of the Solid State," GARNER, *editor*, Butterworths, London, 1955, Chap. 7.

Proceedings of the

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Philosophical Antecedents of the Modern Atom

Mel Gorman
University of San Francisco
San Francisco 17

In their treatment of atomic theory in general chemistry texts, almost all authors include at least a few historical statements outlining Dalton's contributions. Unfortunately, some of these discussions give the impression that the concept of the atom is a product of modern science. This results in a lost opportunity to present to students the existence of the continuity of an idea which first served as an answer to questions of ancient speculative philosophy and which now provides the fundamental framework of modern quantitative science. "No important system of thought has ever appeared in the world as the 'special creation' of its founder, wholly detached from what has gone before: it must have its roots in the speculations and discoveries of many predecessors, which have been advancing unconsciously toward one solution" (*1*). The purpose of this paper is to present a brief survey of Greek atomism, its rise, recession, and revival, with the hope that teachers of general chemistry may wish to incorporate some of this subject into their courses.

Rise of Greek Philosophy

The Greek colonists of Ionia, in Asia Minor, manifested some of the characteristics associated throughout history with colonists of every nation. They were unfettered by traditional influences so that their initiative in every field of endeavor was unrestricted to an extent which they never would have imagined in the homeland. The result was a sociological environment in which any one of the spheres of political, economic, cultural, or intellectual pursuits might have been developed to a high state of refinement. As a matter of fact, the Ionian Greeks reached a high level of civilization generally, but here we shall be concerned only with their intellectual contributions which gave rise to the birth of natural philosophy (*2*), the forerunner of modern science.

It is conceivable that the inhabitants of Ionia, in spite of or because of their comfortably favorable circumstances, would not have had the incentive to exert themselves intellectually, especially to pioneer a new field of thought. Very few ancient civilizations produced any kind of philosophy. But these transplanted Greeks had strong mental powers. Perhaps their most outstanding personal feature was that of enthusiastic curiosity, which led to successive questions of "Why?" in the pursuit of knowledge about any subject. They were keen observers, and after gathering a few facts and making a few inquiries they were capable of making hypotheses and abstractions. They had a gift of impartiality of judgment which they applied not only to their own sociological activities, but also to the world around them. Endowed with these faculties, the Greeks in the sixth century B.C. created an original philosophical science, secular in character because it was devoid of any primitive religious or mythological notions, and remarkably similar to modern science in its fundamental tenets, astonishing even today with its "comprehensiveness of view and an organic cohesion of design" (*3*). "For the first time, the human mind conceived the possibility of establishing a limited number of principles and of deducing from them a number of truths which are their strict consequence" (*4*). For additional background on the rise of Greek philosophy the reader may consult the sources in reference (*5*).

The Problem of the Nature of the World

In boldly embracing the entire world as their problem, the earliest natural philosophers consciously and deliberately addressed themselves to the question: What is the ultimate material substance out of which the world is composed? In following their mental footsteps, it must be realized that, to the Ionians, the most striking characteristic of the world was the perpetual flux of so many things which were important to them—life and death, day and night, storm and calm. The mention of the changing world appears time and again in their literature. Yet these pioneer cosmologists were not satisfied that the answer to their question was simply change itself. They believed that somehow there was something underlying all mutations, something that was primary in itself but which could manifest now one form and now another. Thus, to answer the fundamental question concerning the nature of matter, the first philosophers were confronted with a para-

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doxical problem of their own making—namely, to explain the existence of a ceaselessly changing world consisting of some immutable underlying stuff.

Monists and Pluralists (6)

The first natural philosopher, Thales (c. 624–548 B.C.) of Miletus, Ionia, directed by an intuitive seeking for unity, proposed that water was the primary material of the world. His reasons for arriving at this conclusion have been lost, but they must have taken into account such observations as the abundance of water, its necessity for plants and animals, and its ease of transformation to "air" (water vapor) and "stone" (ice). If water could change into air, it could reconvert to rain, fog, and dew. If it could harden to one kind of stone, then it could have been the source of other hardening processes which resulted in the formation of rocks and other earthy solids. Naïve and fantastic as such an idea appears at present, it was by no means implausible to contemporary philosophers. Far from ridiculing Thales, they adopted the same idea, only making different choices of substance which they regarded as giving a more logical explanation of nature. Anaximines (d. 528 B.C.) believed in air as the fundamental matter, while Heraclitus (c. 500 B.C.) selected fire. These philosophers are grouped as monists.

Monism might have continued on and on in fruitless grasping at one after another primal substance if it were not for the appearance of Parmenides of Elea in Southern Italy, around 500 B.C. To the present-day scientist the views of Parmenides will have an out-of-this-physical-world ring about them. Indeed, they should have, for this philosopher had no intellectual kinship with the natural philosophers of his own day, who were the objects of his attack. He was a metaphysician, concerned not with observations and the appearances of things as such, but with the processes of abstract thought which would yield ultimate truth. Nevertheless, he performed a valuable role in the history of science by cutting short the life of monism, thus removing a roadblock and clearing the way for more reasonable explanations. Without attempting any consistent elaboration of all of his propositions, it is sufficient to say Parmenides maintained that monism had to be interpreted as meaning that the world must be a pure, solid, completely filled continuum. It cannot be divided because then it would be two or more. There could be no transformations because there was no room available into which the new material could fit, and furthermore the disappearance of anything would leave a hole, and this would destroy material continuity. Hence, there can be no motion, change, or anything of a transient nature. But what of the *obvious* changes which can be seen everywhere? This question implies something else that is obvious; namely, according to Parmenides there is a contradiction between logic and the senses, and he had no trouble making his choice. The senses, he said, provided nothing but illusions of change and could not be trusted at all. So rigorous and forceful was his dialectic that Parmenides had a profound effect on the contemporary monists, whom he vanquished by establishing his own version of a rigid and immobile monism. Moreover, all future speculators were warned that their theories must be capable of withstanding the scathing logic of similar sceptics.

Regardless of the admiration for the penetrating analysis of Parmenides, all thinkers did not follow his rejection of the reliability of sense perception, but they did see the shallowness of the monist position, which was now untenable. Another line of attack on the problem of nature was now in order, and it is easy to guess its direction. If one primary substance was insufficient, then the alternative was to have two or more primary substances. Thus was born the school of pluralism. We shall consider as one example the theory of Empedocles (c.492–c.435 B.C.) of Agrigentum in Sicily. This philosopher of nature is bound to appeal to the modern chemist. Empedocles thought and wrote in a manner which closely parallels some of the fundamental concepts of today's chemistry. For instance, he arrived at the notion of an "element," not in the modern sense to be sure, but the idea is still with us. For him there were four elements, air, earth, fire, and water, each of which was uniform and immutable. Any complex natural object would be separated once and then twice or more, but eventually two or more of the elements would be separated, and beyond them no further separation would be possible. Of course, the number of combinations obtainable from just four starting materials is limited. Empedocles obviated this difficulty by establishing a principle of far-reaching influence; namely, combination in varying proportions, thus leaving room for an infinite variety of objects and phenomena. Any seemingly new substance formed is merely the result of the commingling or rearrangement of the elements (a modified conception which we still use with the atoms of modern elements). Besides the four elements Empedocles believed in two other types of matter, "love," which made the elements combine, and "strife," which tended to separate. Although it is difficult to visualize what type of matter he had in mind, nevertheless it is clear that here is the foreshadowing of the concept of chemical affinity.

In spite of the value of Empedocles' theory as attested by the persistence of some of his ideas down to the present, his system as a whole was soon discovered to have some fatal weaknesses. For one thing, why stop at four elements? Five or six would do just as well. Also, if the elements have a fixed nature, they cannot actually produce anything else. Then again, some philosophers yearned for a return to the older basic unity of the world. Another critical milestone in the history of science had been reached. Pluralism died and only the sterile Parmenidean monism remained.

The Great Compromise

The situation was intellectually desperate. For a century the best Greek philosophers of nature had wrestled with the problem of unity versus multiplicity, and in spite of differences, much intellectual maturity had been the result. Must all this now be discarded by the necessity of a new start, with the prospect of another century or so before an equal level of understanding could be reached? Fortunately for the efforts of his philosophical predecessors (and for the advance of experimentation by his scientific descendants many centuries later), this crisis was

eliminated by Leucippus who synthesized the tenets of monism and pluralism into an intelligent coherence known as the atomic theory. Leucippus, probably of the Ionian city of Miletus, lived in the middle of the fifth century B.C. According to his brilliant insight, matter was made of atoms, each one of which was solid, compact, indivisible, eternal, unchangeable, without any internal motion, and of infinitely various shapes; i.e., each one was a homogeneous continuum, and as such would satisfy the most ardent Parmenidean. Pluralism was acknowledged in this theory by having an infinite number of these atoms, although numerically limited in any one thing. One of the accomplishments of Leucippus was his adoption of the concept of space (void or vacuum). In this concept he made a clean break with both previous systems. For him it was impossible to conceive atoms unless they had unoccupied space which separated them and in which they moved with random motion. With this space Leucippus becomes the father of kinetic theory, for he endowed his atoms with an inherent random motion.

How can particles of such uniformity account for the great variety in the world? The natural result of violent randomness of actions is collision followed by recoil with no change save that of a new direction, or by some kind of interchange. The latter was effected mainly by having the atoms of different shape combine to give different resultant compound objects in which the atoms had different relative positions. However, the nature of this union must be understood clearly. Chemists do not have to be informed that in many respects Leucippus' atoms are practically identical with today's atoms. But not so with their combinations. The gist of combination in the original theory is to be found in shape and position. Actually, using the words "combination" or "union" to describe the nature the old interatomic relationships is reading too much of modern chemistry into the ideas of Leucippus. It is better to use the description of his contemporaries and immediate successors. They used the word "entanglement," or "interlacement" with the connotation that atoms of complementary shape could "come together" much as a worn key can be placed in a lock without actually touching the latter. Two inferences are involved. Neither the key nor the lock is changed and there is space between them to provide room for a constant vibratory motion. If the atoms were changed, the very foundation of the theory would be invalidated; space is needed between the adjacently fitted atoms to account for transformations of complex objects. One of the many atoms freely moving in space may strike a compound substance, and if the symmetry of the free atom and those in the compound are favorable, the new atom will be "taken in" to form a more complicated aggregate. But if any unsuitable atom is involved, it may force its way into the interstitial space between atoms of a compound body and split the latter asunder, either converting it completely into atoms or partially into simpler substances. By such postulates Leucippus claimed that the great variety of transformations observed in nature could be accounted for in a rational manner. Another feature of combinations is the postulate that the everlasting motion of the atoms is not quieted by the formation of compound bodies. The interlocked atoms are in a state of constant vibratory motion.

No Greek philosopher worthy of the name ever thought of a limited system of thought. Natural philosophers, for the most part, were inclined to believe that practically everything was material in nature, and in this tradition we find Leucippus extending his theory to the soul, the mind, the senses, things which are beyond the scope of physical scientists.

Democritus

Democritus (c.460–c.370 B.C.) was born in the Thracian city of Abdera and was a pupil of Leucippus. He travelled widely and spent long sojourns in foreign lands for the purpose of study. He became a universal scholar of great erudition, and he was able to take the atomic theory of Leucippus and cast it within the framework of the whole scope of human knowledge. The theory was not substantially revised by Democritus, but he did strengthen it by making it more systematic and explicit, and he extended it by a more penetrating and imaginative insight. Democritus sets forth in no uncertain terms that the world of atoms is uncreated, eternal, deterministic, and mechanistic. The atoms are not ruled by any external design or force but operate according to their own natural law. He wished to eliminate the possibility that any slightly surviving religious or mythological principles would ever creep into his system and stamped it as a purely naturalistic philosophy. As far as modern chemical theory is concerned, Democritus did not contribute much more than Leucippus. The genius of Democritus manifested its greatest versatility in those fields which today belong to disciplines other than chemistry. Principles and observations in such diverse fields as astronomy, physics, cosmogony, epistemology, theology, psychology (*7*), physiology, and zoology were accounted for directly or indirectly in terms of the atomic theory.

Reaction to Atomism

In spite of the great intellectual reputation of Democritus, his atomic theory never enjoyed widespread acceptance. He must have had some adherents, but they must have been obscure men unworthy of historical preservation. The primary reason for this unenthusiastic reception was the concurrent rise of sophism, an intellectual movement which turned the attention of man from his natural environment to himself as a moral, logical, cultural, and political entity (*8*). One of the underlying tenets of sophism embodies a scepticism toward many traditional concepts, including the validity of sense perception. The sophists were itinerant and aggressive teachers, and in their path atomism soon was flattened. Socrates (470–399 B.C.), the ethician, and Plato (428–348 B.C.), the idealist, disdained science. But as time went on, sociological conditions changed (*9*) so that the Hellenic mind was capable of return to things of science. This movement was implemented by Aristotle (384–323 B.C.), although he rejected atomism for explanations of his own. Yet the current scene demanded

a materialism which would appeal to the man in the street and at the same time provide him with a personal and individual code of morality.

Epicurus

The required conditions were fulfilled in the philosophy of Epicurus (341–270 B.C.), whose school in Athens was the source of an evangelistic missionary moralism. Epicurus reversed the scepticism of the sophists by restoring the validity of the senses, and he elevated nature above reason as a criterion for judgment and action (*10*). Of course, such a basis required a thorough knowledge of man's physical environment, and for Epicurus this was found in the atomism of Leucippus and Democritus. Epicurus revised, extended, and unified the theory to suit the requirements of his moral philosophy. Of interest to modern chemists is the addition of weight to the primary characteristics of atoms. Because of this weight, free atoms had a different kind of motion than previously thought. Epicurus maintained that free atoms were falling perpendicularly in the void due to their weight. Various atoms had different weights but all moved with the same speed. Atomic aggregates were formed because by pure chance the atoms deviated from their perpendicular paths and underwent collisions to form compound bodies as in the older theory (*11*).

Epicureanism enjoyed a phenomenal success. It spread all over the civilized world and flourished well into the Christian era. This was due to the fact that it had a common sense appeal to the average man. But atomism was always in the distant background and was espoused by only a few intellectuals. The outstanding example of the latter is Lucretius (c. 99–c. 55 B.C.) (*12*), Roman poet and Epicurean who wrote the great didactic epic, *De Rerum Natura* (*On the Nature of Things*). This is a faithful portrayal of Epicurus, and hence, essentially, of Democritus and Leucippus and is our chief source of knowledge of ancient atomism. Lucretius beheld the action of atoms as actors on the stage of the infinite void, and he described the theory with an enthusiastic poetic eloquence. His poem is one of the few works which can be read for its literary style and scientific content. A prose translation (*13*) on the kinetics of atoms is a source of admiration and delight for the modern scientist.

Fate of Philosophical Atomism

We have seen that the atom, as an intellectual concept, played only a minor role in the broad acceptance of Epicureanism. In spite of its vigor, this philosophy eventually succumbed to a disorganized but persistent effort of Platonists, Aristotelians, Stoics, Christians, and Jews, who objected to its materialistic and anti-theological tenets. By A.D. 400 Epicureanism was a pile of philosophical rubble, and its atomism was buried at the bottom of the heap. In the meantime, Galen (c. A.D. 130–A.D. 200), second only to Hippocrates in reputation, expelled atomism from medicine because its mechanistic explanations of such a marvelous complex as the living body seemed woefully inadequate (*14*).

It is sometimes stated that atomism was dead for a thousand years finally to be resurrected by modern science. However, it is difficult to bury an idea even for a short time; the concept of the atom went into a deep recession, but it did not expire. In practically every century there is some mention of atomism, however slight, either to praise it or condemn it, but mostly the latter. For instance, in the Middle Ages a long list of European churchmen, grammarians, lexicographers, and encyclopedists discuss Epicurus and Lucretius (*15*) from one point of view or another. During this time the center of intellectual activity had migrated to the east, and here we find atomism on a much wider scale, with extensive works of its Saracen and Jewish champions and detractors (*16*). In the fifteenth and sixteenth centuries there was a quickening of atomic interest (*17*), which culminated in a full-blown revival in the seventeenth century.

Revival and Growth of Atomism

The most prominent reviver of atomism was Pierre Gassendi (1592–1655) (*18*), who played the dual role of christianizing the atomic theory of Epicurus and then popularizing it for scientific acceptance. Gassendi adopted the materialism of Epicurus while rejecting its atheism and professed that the atoms were created by God. He was able to convert others to this modified Epicurean atomism by the sheer force of his intellectual and personal characteristics. A mere partial tabulation of the man's qualities and activities—dignified priest and theologian, revered man of the world, literateur and biographer, respected adversary of Descartes, courageous comforter of Galileo, philosopher, anti-Aristotelian, astronomer, experimenter in acoustics and mechanics—indicates the fact that he moved with ease in scientific, philosophical, and theological circles. As a result of his efforts, atomism became not only acceptable, but even fashionable. Of prime interest, however, is the fact that Gassendi's espousal of atomism provided the new science with a philosophical context which previously had been lacking. Subsequent history has shown how fruitfully this ancient philosophical notion has grown in the soil of modern science.

Although bringing Greek atomism within the confines of orthodox Christianity and inventing some new arguments in its support, Gassendi made no new contributions to the theory. Improvement along these lines had to await the minds of more able scientists. But even here Gassendi's influence was felt, because he provided a theologically satisfying atomic system and cleared the way for the use of the atom by men of religious bent like Boyle (1627–91) and Newton (1642–1727). Space does not permit an account of the mode of his influence on these two scientists, and their role in the history of atomism is treated elsewhere (*19*). It is sufficient to state here that after the impetus provided by Gassendi and accelerated by Boyle, Newton, and others, the theory of atoms spent almost all of the eighteenth century wending its tortuous way through the theories of phlogiston and chemical affinity before it found itself in the era of modern science following the chemical revolution brought about by Lavoisier (1743–94). One of Lavoisier's great contributions was the demonstration of the power of the quantitative approach to chemical

problems. It was in this intellectual climate that Dalton (1766–1844) converted atomic concepts of his time into the quantitative expression of the modern atomic theory. Contemporary modifications of the Daltonian atom have been made, and more will come. Nevertheless, extremely wide areas of phenomena classified under many individual sciences can be treated within the conceptual framework provided by Dalton and his many predecessors.

In the present educational climate it seems unnecessary to defend the thesis that scientists tend to become engrossed in their own narrow specialties, a condition which results in loss of perspective regarding other fields (*20*). It is the duty of teachers to see that tomorrow's scientists are not burdened with this stigma. Recent statements have expressed the situation succinctly. "The teacher who shows... the relation of science to other disciplines can help a good deal in reducing intellectual provincialism among his students" (*21*). "Scientists must learn to teach science in the spirit of wisdom and in the light of the history of human thought and human effort" (*22*). "Science is taught often in a dull way. Students learn it as a ready-made object and have no conception of science as a living thing with laws of growth and decay. For a true understanding of his own science, the young student must learn how principles and theories have developed" (*23*). "... there is little opportunity for introducing courses in the history and philosophy [of science] into ... crowded curricula. Hence emerges the importance of history and philosophy as ingredients in the teaching of the sciences themselves" (*24*). The author of this paper considers the above citations[1] to be a reasonable basis for urging that at least a survey of the philosophical antecedents of atomism be considered in the general chemistry course prior to presenting the Daltonian atom.

[1] These quotations are taken from papers delivered at a conference on the history, philosophy, and sociology of science sponsored by the American Philosophical Society and the National Science Foundation. I am indebted to Dr. Joel Hildebrand for calling these references to my attention.

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Sources of Information on Careers in Scientific Fields

The Manufacturing Chemists' Association has prepared a pamphlet listing a selected bibliography of career information. It should be in the hands of every guidance counselor in the country. It provides help in selecting a career-counseling library and generally answers the many forms of the question, "Where can I find out about what a scientist does?"

MCA will provide 6 copies free; additional copies, five cents each. Write 1825 Connecticut Ave., N.W., Washington, 9, D.C.

Report of the New England Association of Chemistry Teachers

Jay A. Young
King's College
Wilkes-Barre, Pennsylvania

Practice in Thinking

A previous publication[1] described a new approach to the elementary laboratory. Laboratory problems, from simple to complex, are assigned to each student or pair of students. They solve an assigned problem by developing and testing a hypothesis related to the phenomena observed when the steps described in their problem are carried out in the laboratory. The major emphasis is placed upon the conception of a plausible, testable hypothesis, and upon the procedural steps taken to carry out the test.

In general, students respond well to this approach since it gives them an opportunity to meet a challenge that is within their ability to surmount. The answers to the assigned problems are not furnished directly by a laboratory manual or on a previously specified page of a text or reference book. Hence the students must read rather widely and diligently to find the desired information. As a result information is learned; some real thinking is done, both in the conception of a testable hypothesis and in the effort to devise a test of the hypothesis.

Examples of the problems assigned to students have been given in the previous publication[1] and a complete list of problems is available[2] but one example can be cited here. A small piece of aluminum foil is cleaned with benzene to remove any residual grease that may be present on its surface and is then burnished lightly with steel wool. The foil is partially immersed in a solution of mercury(II) chloride and, upon removal from this solution, a white growth forms on the foil. The student is asked to explain why a white growth forms on the foil (he is not told that the white substance is aluminum oxide; this is left for him to find out by further study).

The observed phenomenon is sufficiently interesting in itself to excite the curiosity of all but the dullest students. The typical student will readily turn to his text and other available references in an effort to find an explanation. Usually, the explanation offered hinges upon the statement that some of the mercury(II) chloride is reduced by the aluminum, and the mercury, so formed, amalgamates with the aluminum in the foil. The amalgamated aluminum then reacts with the oxygen in the air to form white aluminum oxide.

There are several possible tests for this hypothesis, of course. A student can show by qualitative tests that aluminum will indeed reduce mercury(II) ions while it is itself oxidized. Or, the existence of an electromotive force, in the proper direction, generated by the $Al\text{-}Hg^{++}$ couple can be confirmed. Or, as one student suggested, the change in weight of the aluminum foil, after a few minutes immersion in the mercury(II) chloride solution, can be measured, and after suitable heating to drive off the mercury residing in the foil, the weight redetermined.

From data such as these the student who attempted this approach hoped to show that the weight of mercury that amalgamated with the foil was chemically equivalent to the loss in weight of metallic aluminum. The procedure was not effective because aluminum oxide formed on the foil while it was being weighed. In a second attempt, the amalgamated foil was placed in a conical flask and the flakes of white substance were collected and saved as the reaction proceeded. Ultimately, the residual, unreacted aluminum was weighed and the weight of aluminum present in the white substance determined by a colorimetric measurement. The weight of aluminum found in the flakes agreed within 5% with the loss in weight of the foil. In a third attempt, a stoppered conical flask was used, and the weight of aluminum in the white substance, assuming it to be aluminum oxide, agreed within 3% of the calculated quantity of oxygen present in the air in the stoppered flask.

Although the original hypothesis was not thoroughly tested by this procedure, the results of the tests that were performed did not contradict the hypothesis. The student concluded that his hypothesis was valid within the limitations of his investigation and turned his attention to another assigned problem.

This student learned more about the chemistry of aluminum, colorimetry, the behavior of gases, and other topics than has been indicated explicitly here since he necessarily studied many texts and references in order

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Adapted from the Shawinigan lecture presented during the twenty-first annual summer conference of the NEACT, August 17–21, 1959, at the University of Connecticut, Storrs.

[1] Young, J. A., J. Chem. Educ., **34**, 238–9 (1957).

[2] Young, J. A., "Practice in Thinking," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1958.

to acquire the information that was used to form his hypothesis and to test it in the laboratory. Although he did discuss his problem with several of his classmates and upperclassmen, he did not seek specific help from these others. This action is typical; students sense a personal challenge and seek only generalized assistance from others. In this case, since the student was unaware of the technique, the only specific recommendation received was from the instructor, who hinted that aluminum might be determined colorimetrically. This suggestion was not requested by the student until he had, himself, found that the amount of aluminum oxide formed in his procedure was too small to determine gravimetrically with sufficient precision.

The student had previously worked on other, less complicated problems. It has been found that poor students are discouraged by a problem of this complexity when it is assigned to them as the first or second problem to be solved. Since students of limited ability cannot easily be identified early in the year, the complete list of problems for which a student is responsible is assigned to him in the beginning of the semester; at least two of these problems are not complicated. The more proficient students usually solve these quickly and proceed to more advanced challenges. Students of average ability find their experience with the simpler problems helpful since usually all they need is personal experience with a method of approach that is so very new to them. Once they understand the general approach to be used in solving a problem they are able to continue at a satisfactory pace, occasionally surpassing their originally more proficient classmates.

The very poor students show up sharply as poor students. When a cook-book, fill-in-the-blank manual is used the poorer students can often bluff their way through the laboratory. This is not possible with this procedure and, were it not for the fact that some of the more glaring deficiencies of the poorer student are brought to light by this method, the results with poor students would be very discouraging indeed. At it is, however, because their weaknesses are clearly exposed to the instructor, some of the poorest students can be helped, if not to continue in chemistry, at least to continue in some other major study for which they are better fitted but in which they might well have failed had their habits of study and reflection not been corrected.

It is a platitude that a teacher cannot force learning upon a student. Somehow, the student must be persuaded to teach himself. Basically, the method described here depends upon the principle that man, by nature, is curious and that a challenge that excites curiosity can be given, even to a beginning student. And if the student himself can foresee that the challenge is not beyond his ability to solve, he will meet it successfully and will learn in the process. The teacher's task is thereby reduced to its proper dimensions, to guide the order of acquisition of knowledge in accordance with the progress of the student as he learns.

It is also a platitude to state that it is unrealistic and improper to allow the student to infer, from the methods we use in teaching, that chemistry is best learned by rote and by cook-book methods. The student must learn that chemistry is a vital, real subject, in which many answers are still unknown. Perhaps the beginning laboratory course has been the greatest offender in this respect, but it is also true in some other courses that we teach. What has been outlined here is only a beginning. A similar approach can be used in other courses.

Chem Ed

LETTERS

To the Editor:

The very interesting paper by G. R. Choppin (J. CHEM. EDUC., **36**, 462 (1959)) contains data about the adsorption of Pa, U, Np, and Pu on an anion exchange resin, Dowex-1, from hydrochloric acid, collected in Table 1. Similar data, although numerically somewhat different, appear in Table 7.9, page 264, of the book by Katz and Seaborg, "The Chemistry of the Actinide Elements," John Wiley & Sons, Inc., New York, 1957. Neither author gives references to the sources of the data. Now it appears that some of the entries are erroneous, because of changes in oxidation state of the actinide ion during equilibration with the resin through disproportionation or reaction with the resin or impurities.

Work done at Oak Ridge National Laboratory (ORNL 2584), under conditions where the oxidation state could be definitely ascertained spectrophotometrically, gave the following results. Defining "strong adsorption" as volume distribution coefficients above 10, then the lower limits of hydrochloric acid for observing "strong adsorption" are U(IV) 8*M* (or 10*m*), U(VI) 2*M*, Np(IV) 6*M* (or 7*m*), Np(V) not adsorbed at any concentration, Np(VI) 1.5*M* Pu(III) not adsorbed at any concentration, Pu(IV) 6*M* (or 7*m*), Pu(VI) 1.7*M*. The facts to emphasize are that the hexavalent state is in all cases much more strongly adsorbed than the tetravalent state, and that the tri- and pentavalent states of U, Np, and Pu are not adsorbed at all from hydrochloric acid.

These results were presented more fully at the XVIIth Congress of IUPAC at Munich, August-September, 1959.

Y. MARCUS

ATOMIC ENERGY COMMISSION LABORATORIES
REHOVOTH, ISRAEL

Chem Ed

BOOK REVIEWS

The Molecular Basis of Evolution

Christian B. Anfinsen, National Heart Institute, Bethesda, Md. John Wiley & Sons, Inc., New York, 1959. xiii + 228 pp. 96 figs. 15 tables. 15.5 × 23.5 cm. $7.

One of the great scientific developments of our time is in the field now frequently called molecular biology, which is deepening and transforming our understanding of evolution and genetics by studies of the fine structure of nucleic acids and proteins, and relating them to the differences between individuals and between species. Genetics, which developed as a rigorous science with its own set of concepts such as the gene, has now become completely interwoven with modern biochemistry.

This book by Anfinsen is a major contribution to the broader diffusion of knowledge about molecular biology. It is addressed to readers with a reasonably good knowledge of organic chemistry, but it assumes that the readers may know very little of evolutionary biology or of genetics. The author is a distinguished biochemist who acknowledges that a few years ago he had little familiarity with the latter subjects. Since then he has amply remedied this deficiency and in his opening chapters he sets forth some of the basic facts about evolution and genetics—facts which are unfortunately still too little known to many modern chemists. In his third chapter, on the chemical nature of the genetic material, he comes to grips with the structure of DNA, which has been dramatically clarified, notably by Watson and Crick. Chapter 4 takes up the substructure of genes and reviews the remarkable work of recent years which shows that mutations may and do occur in minute regions of the genetic material corresponding to one or to only a few nucleotide units of the DNA. This leads, in chapter 5, to a valuable discussion of protein structure, which sets forth the fundamental physical properties of peptide chains, the ways in which they can coil and twist, and the revolutionary work which has given complete and detailed information about the amino acid sequence in molecules as large as ribonuclease, with 124 amino acid residues linked in a chain which is further cross-linked by four disulfide bonds. X-ray diffraction analysis is now giving a detailed picture of protein molecules such as myoglobin, revealing extraordinary twists and convolutions of the peptide chain, the biological significance of which is still to be discovered. Chapter 6 deals with the problems of biological activity of proteins in relation to structure. In the present state of our knowledge it is necessarily fragmentary and speculative, but is highly suggestive. Chapter 7 discusses species variations in protein structure, a rapidly expanding subject with vast implications for the biology of the future, and the following chapter considers genes as determinants of protein structure, including such dramatic correlations between genetics and biochemistry as the small but specific chemical changes in various kinds of human hemoglobin that are associated with specific mutations. Small as these chemical changes are, they may make the difference between life and death to the individual who carries the mutation, as in the well known case of sickle-cell hemoglobin. Chapters 9 and 10 consider the mechanism of protein biosynthesis, a rather brief and sketchy treatment of a very rapidly growing field, and the degree of accuracy with which proteins of precisely defined structure can be manufactured by the biosynthetic process. The last chapter, Genes, Proteins, and Evolution offers a view of achievements with perspectives for the future.

This book deals with problems, on the frontiers of science, that are intellectually fascinating and are also of the most vital importance to anyone who cares about the future of mankind and other organisms on this planet. It should open new scientific vistas for many readers, and I trust that it will arouse gifted young investigators to tackle some of the many profound and exciting problems that still remain to be solved.

JOHN T. EDSALL
Harvard University
Cambridge, Massachusetts

Principles of Chemistry

Donald C. Gregg, University of Vermont. Allyn and Bacon, Inc., Boston, 1958. xx + 600 pp. 85 figs., 35 tables. 16 × 23.5 cm. $6.50.

This textbook is quite scholarly and demonstrates that there is one more way of planning a textbook for a course in modern chemistry. True to its title, it emphasizes the principles of chemistry. The book consists of 24 chapters averaging 23 pages each. Chapter 22 is entitled Oxygen, and Chapter 23 deals with hydrogen; no other chapter is devoted to an element, or even to a group of elements, as such. Descriptive chemistry is skillfully interwoven throughout the book but is featured to a lesser extent than the fundamental concepts that are used to interpret and predict chemical phenomena.

In fifteen pages, water is treated as a Brönsted acid and a Brönsted base; in twelve more pages it is considered as a Lewis base. In the course of this discussion, much is necessarily said about various elements and compounds.

The expression for the equilibrium constant for a reversible reaction is derived in this text in the traditional manner, i.e., by equating rate expressions for the forward and reverse reactions that are based on stoichiometry. This derivation is valid only in exceptional cases, e.g., the hydrogen-iodine-hydrogen iodide equilibrium. A more valid approach, taken by only a few authors to date, is to present the expression for the equilibrium constant as a statement of experimental fact. Consideration of the rates and mechanisms of reactions need not—perhaps should not—precede the treatment of chemical equilibrium.

The book contains 25 photographs, including a frontispiece and one at the beginning of each chapter. The text is adequately illustrated with drawings, including representations of molecular models.

At the end of each chapter is a set of carefully constructed problems, many of them numerical. Answers to numerical problems are given at the back of the book.

A list of suggested readings, classified by subjects, is provided at the end of the book. The references are to books and

Reviewed in This Issue

Christian B. Anfinsen, The Molecular Basis of Evolution
Donald C. Gregg, Principles of Chemistry
I. M. Kolthoff and *Philip J. Elving*, Editors, assisted by *Ernest B. Sandell*, Treatise on Analytical Chemistry. Volume 1 of Part 1, Theory and Practice.
Ibert Mellan, Source Book of Industrial Solvents. Volume 3, Monohydric Alcohols
Alfred B. Searle and *Rex W. Grimshaw*, The Chemistry and Physics of Clays and Other Ceramic Materials
Andre Maurois, The Life of Sir Alexander Fleming. Translated by *Gerard Hopkins*
E. A. Coulson and *E. F. G. Herington*, Laboratory Distillation Practice
G. Malcolm Dyson, A Short Guide to Chemical Literature
H. H. Neville and *W. E. Yuill*, Translation from German for Chemists
Louis F. Fieser and *Mary Fieser*, Steroids

journal articles, with THIS JOURNAL receiving most frequent mention.

Examination of the very complete index will prove the author's statement that considerable descriptive chemistry is contained in this book. Its placement and quantity, the author concedes, may seem unorthodox. Teachers are expected to add more descriptions of their own choice and to omit those theoretical topics which they do not wish to discuss.

LAWRENCE P. EBLIN
Ohio University
Athens, Ohio

Treatise on Analytical Chemistry. Volume 1 of Part I, Theory and Practice

Edited by *I. M. Kolthoff*, University of Minnesota, and *Philip J. Elving*, University of Michigan, with the assistance of *Ernest B. Sandell*, University of Minnesota. Interscience Publishers, Inc., New York, 1959. xxvi + 809 pp. Figs. and tables. 17 × 24 cm. Single copy, $17.50. This volume by subscription, $15.

As stated in the opening sentence of the Preface, "The aims and objectives of this Treatise are to present a concise, critical, comprehensive, and systematic, but not exhaustive, treatment of all aspects of classical and modern analytical chemistry." This aim is ambitious indeed, but the experience, competence, and enthusiasm of Professors Kolthoff, Elving, and Sandell is such that the probability is high that it ultimately will be achieved.

The intention is to publish the Treatise in three parts: Part I, Theory and Practice; Part II, Analytical Chemistry of the Elements; and Part III, Analysis of Industrial Products. Each of these parts will comprise many volumes. The three parts will not be published *seriatim*, but concurrently volume by volume.

The present volume is the first of Part I, it is only the beginning and yet comprises 809 pages! Its nineteen chapters and their authors are as follows: Methods of Analytical Chemistry (Ernest B. Sandell and Philip J. Elving), Errors in Chemical Analysis (Sandell), Accuracy and Precision (W. J. Youden), Principles and Methods of Sampling (William W. Walton and James I. Hoffman), Elements and Compounds (James I. Watters), Atomic Weights (Edward Wichers), Chemical Equilibrium and the Thermodynamics of Reactions (T. S. Lee), Graphic Presentation of Equilibrium Data (Lars G. Sillen), Electrode Potentials (Roger G. Bates), Concept and Determination of *p*H (Roger G. Bates), Concepts of Acids and Bases (I. M. Kolthoff), Acid-Base Strength and Protolysis Curves in Water (Stanley Bruckenstein and Kolthoff), Acid-Base Equilibria in Nonaqueous Solutions (Kolthoff and Stanley Bruckenstein), Complexation Reactions (Anders Ringbom), Mechanisms of Oxidation-Reduction Reactions (Fredrick R. Duke), Oxidation-Reduction Equilibria and Titration Curves (Duke), Solubility (D. L. Leussing), Precipitates: Their Formation, Properties, and Purity (Murrell L. Salutsky), Equilibria in Precipitation Reactions, and Precipitation Lines (J. F. Coetzee). Analytical chemists will recognize many of their most respected colleagues and friends from related fields among these authors, and will not be surprised at the general excellence of the text.

The volume has been edited with care and skill so that it is remarkably uniform in spite of the many authors that have contributed to it. The only glaring editorial fault—and in my opinion it is a serious one—is that literature references are grouped together at the end of each chapter. Such a nice, neat orderly list gladdens the heart of a copy editor, but it is a very real annoyance to have to keep paging back and forth between references and text. In a reference work of this kind literature citations ought to be a living part of the text, and therefore they should be placed where they can be used efficiently and easily, namely, as footnotes on each page.

There certainly is real need for an authoritative, comprehensive treatise on analytical chemistry. However, because the theory and general practice of analytical chemistry already are treated at least fairly adequately in existing special monographs, the need for Part I of the present Treatise is not nearly as urgent as for the planned Parts II and III. In my opinion this Treatise will make its greatest contribution to its subject in Part II on the Analytical Chemistry of the Elements, and I look forward eagerly to the appearance of the volumes of this part.

JAMES J. LINGANE
Harvard University
Cambridge, Massachusetts

Source Book of Industrial Solvents. Volume 3, Monohydric Alcohols

Ibert Mellan, Polychrome Corp., Yonkers, New York. Reinhold Publishing Corp., New York, 1959. vi + 276 pp. 57 tables. 16 × 23.5 cm. $10.

This book is just what its title implies. It will be useful for the industrial chemist who needs to be reminded in the introduction that "alcohols are secondary when they contain the group—CHOH joined to two radicals." See also THIS JOURNAL 35, 370 (1958).

W. F. K.

The Chemistry and Physics of Clays and Other Ceramic Materials

Alfred B. Searle and *Rex W. Grimshaw*. 3rd ed. Interscience Publishers, Inc., New York, 1959. 942 pp. Figs. and tables. 16.5 × 23.5 cm. $16.25.

Although nominally a third edition of the book of the same title which appeared 25 years ago this treatise has been so extensively revised and rewritten that it is really an entirely new book. Because of the rapid development and diligent application of new methods of research it has now become possible to explain much of the art of ceramics in physicochemical terms, a point of view which is properly stressed in the present volume. Consequently it will be of great value not only to the practical man interested in the technology of ceramic manufacture but also to the student or teacher looking for examples of fruitful application of fundamental concepts to problems of genuine industrial importance.

The scope of the book is comprehensive. The 220 illustrations and 173 tables worked smoothly into the clearly written text provide easy access to detailed information which is otherwise frequently hard to locate. Here is much valuable reference material for instructors responsible for advanced courses in colloid or inorganic chemistry, crystallography, mineralogy, or phase rule, as well as for chemical engineers interested in industrial technology or ceramists seeking answers to specific problems. Abundant references are provided to facilitate further detailed study.

Naturally any book which attempts such comprehensive coverage is bound to be somewhat uneven in its treatment of different topics. It is very helpful to have a clear presentation of the geometry of packing, coordination numbers, and the nomenclature and elements of crystallography preceding the discussion of the crystal structure of the clay minerals and methods for their identification. However, the treatment of colloid chemistry is relatively inferior, stopping with the old ideas of lyospheres, and taking no cognizance of modern Dutch and Russian work on the origin of the forces between colloidal particles, nor of American work relating sedimentation volume and rheological behavior to the size and shape of the constituent particles, and the type of packing structure or coordinated network which they form. The section on phase diagrams is excellent but the chapter on Equilibrium State and Physico-Chemical Reactions, although intended to provide a theoretical background for discussion of physical and chemical changes occurring in clay systems, is in reality a superficial review of general physical chemistry which is better presented elsewhere, as in Glasstone's treatise. Occasionally erroneous statements creep in, as the assertion on page 74 that van der Waal's forces are due to the setting up of permanent dipoles in adjacent molecules, or the presumed implication on page 616 that the rate of reaction is related to the magnitude of the energy change.

Although the authors have obviously made a deliberate attempt to include references to American as well as British sources the fact remains that the bulk of the illustrative material is of British origin. Although earlier papers of Grim, Hendricks, etc., are cited there is little or no note taken of their recent work nor of that of van Olphen, Marshall, Bradley, and other distinguished investigators. Parallel references to standard American sources as well as to British authorities, as in the discussion of analysis and chromatography on page 216, would increase the utility of the book in this country. Likewise incorporation in the tabular material of characteristics of clay deposits and their properties from United States,

(*Continued on page A104*)